MAR 20 1924

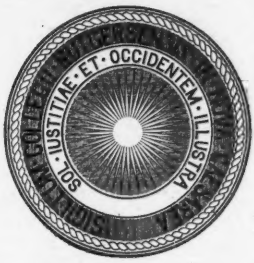
VOL. XVII FEBRUARY, 1924 No. 2

SOIL SCIENCE

FOUNDED BY

RUTGERS COLLEGE

NEW BRUNSWICK, N. J.



JACOB G. LIPMAN, Editor-in-Chief
Assistant Editors
CARL R. WOODWARD
CHARLES A. DOEHLERT

IN CONSULTATION WITH

DR. F. J. ALWAY
University of Minnesota, St. Paul, Minn.
PROF. C. BARTHEL
Centralanstalten för Försöksväsendet på Jordbruksområdet, Stockholm, Sweden
PROF. A. W. BLAIR
Rutgers College, New Brunswick, N. J.
DR. P. E. BROWN
Iowa State College of Agriculture, Ames, Iowa
ALBERT BRUNO
Ministry of Agriculture, Paris, France
DIRECTOR H. R. CHRISTENSEN
Statens Planteavls-Laboratorium, Lyngby, Denmark
DR. H. J. CONN
New York State Experiment Station, Geneva, N. Y.
PROF. DR. H. VON FEILITZEN
Centralanstalten för Försöksväsendet på Jordbruksområdet, Stockholm, Sweden
DR. E. B. FRED
University of Wisconsin, Madison, Wis.
DR. J. E. GREAVES
Utah Agricultural College, Logan, Utah
DIRECTOR ACH. GREGOIRE
Agricultural Experiment Station, Gembloux, Belgium
DR. R. GREIG-SMITH
Linnean Society, Sydney, New South Wales
DR. B. L. HARTWELL
Rhode Island Experimental Station, Kingston, R. I.
DR. D. J. HISSINK,
Agricultural Experiment Station, Groningen, Holland
DR. C. B. LIPMAN
University of California, Berkeley, Calif.
DR. BURTON E. LIVINGSTON
Johns Hopkins University, Baltimore, Md.
DR. F. LÖHNIS
U. S. Department of Agriculture, Washington, D. C.
DR. T. L. LYON
Cornell University, Ithaca, N. Y.
DR. M. M. MCCOOL
Michigan Agricultural College, East Lansing, Mich.
DR. W. H. MACINTIRE
Tennessee Experiment Station, Knoxville, Tenn.
DR. E. A. MITSCHERLICH
University of Königsberg, Prussia
PROF. C. A. MOOERS
Tennessee Experiment Station, Knoxville, Tenn.
DR. THEO. REMY
Institut für Boden- und Pflanzenbaulehre, Bonn a. Rh.
PROF. G. ROSSI
Royal Agricultural High School in Portici, Naples, Italy
DR. E. J. RUSSELL
Rothamsted Experiment Station, Harpenden, England
DR. O. SCHREINER
U. S. Department of Agriculture, Washington, D. C.
DR. ALEXIUS A. F. DE 'SIGMOND
Royal Joseph University of Technicology, Budapest, Hungary
PROF. CHAS. E. THORNE
Ohio Experiment Station, Wooster, Ohio
PROF. N. M. TULAIKOV
Agricultural Experiment Station, Saratov, Russia

PUBLISHED MONTHLY BY
WILLIAMS & WILKINS COMPANY
BALTIMORE, MD., U. S. A.

Entered as second-class matter May 12, 1919, at the post office at Baltimore, Maryland, under the act of March 3, 1879

Copyright 1924, by Williams & Wilkins Company

Price per volume, net post paid { $5.00, United States, Canada, Mexico, Cuba
$5.50, other countries

Made in United States of America

SOIL SCIENCE

Contents for February, 1924

R. V. ALLISON. The Effect of Aeration Upon the Development of Barley in a Heavy Clay Soil 97

ALFRED P. DACHNOWSKI. The Stratigraphic Study of Peat Deposits..... 107

GEORGE JOHN BOUYOUCOS. Effect of Ignition at Various Temperatures Upon Certain Physical Properties of Soils..... 135

SELMAN A. WAKSMAN AND ROBERT L. STARKEY. Microbiological Analysis of Soil as an Index of Soil Fertility: VII. Carbon Dioxide Evolution 141

D. J. R. VAN WIJK. The Quantitative Determination of Nitrates in Soil..... 163

THE WILLIAMS & WILKINS Company – BALTIMORE

Publishers of Scientific Journals and Booksellers

MOUNT ROYAL and GUILFORD AVENUES, BALTIMORE (Maryland, U. S. A.).

"SCIENTIA" **INTERNATIONAL REVIEW OF SCIENTIFIC SYNTHESIS**
Published every month (each number containing 100 to 120 pages)
Editor: EUGENIO RIGNANO

IS THE ONLY REVIEW the contributors to which are really international.
IS THE ONLY REVIEW that has a really world-wide circulation.
IS THE ONLY REVIEW of scientific synthesis and unification that deals with the fundamental questions of all sciences: the history of the sciences, mathematics, astronomy, geology, physics, chemistry, biology, psychology and sociology.
IS THE ONLY REVIEW that by means of enquiries among the most eminent scientists and authors of all countries (*On the philosophical principles of the various sciences; On the most fundamental astronomical and physical questions of current interest, and in particular on relativity; On the contribution that the different countries have given to the development of various branches of knowledge; On the more important biological questions, and in particular on vitalism; On the social question; On the great international questions raised by the World War*), studies all the main problems discussed in intellectual circles all over the world, and represents at the same time the first attempt at an international organization of philosophical and scientific progress.
IS THE ONLY REVIEW that among its contributors can boast of the most illustrious men of science in the whole world. A list of more than 350 of these is given in each number.
The articles are published in the language of their authors, and every number has *a supplement containing the French translation of all the articles that are not French.* The review is thus completely accessible to those who know only French. (*Write for a gratis specimen number* to the General Secretary of "Scientia," Milan, sending 1 sh. in stamps of your country, merely to cover postal expenses).

SUBSCRIPTION: Sh. 40; $10, post free **OFFICE: Via A. Bertani, 14 - Milan (26)**

General Secretary, DR. PAOLO BONETTI

THE EFFECT OF AERATION UPON THE DEVELOPMENT OF BARLEY IN A HEAVY CLAY SOIL[1]

R. V. ALLISON[2]

New Jersey Agricultural Experiment Stations

Received for publication July 14 1923

In studies recently carried out in the laboratories at this station upon the deflocculating effect of fertilizer salts, one of the points that has been particularly emphasized in the relation of this tendency to plant growth is the effect of an increase in aeration or oxygen supply in the substratum. The marked response of the plants studied in artificial culture (1, 2) to the aeration of the substratum made it desirable to investigate the same relation in the soil. Results should directly aid the study of cultural or fertilizer practices which tend to render the soil mass more compact and less pervious to the ready movement of both air and water.

After a ten year period of experimentation, Lipman and Blair (5), found that, within certain limits the dilution of a heavy loam with sand gives a consistent increase in crop production due, without doubt, to superior aeration. Considerable other data upon the fundamental importance of soil aeration are available. Thus, Howard (4) dealing extensively with the pathogenic side of the question indicates the important bearing of aeration upon certain pathological conditions commonly found among the agricultural plants of that section.

In the present studies with soils the treatments were made according to the same scheme as was earlier used in solution cultures (2). Accordingly, it was found necessary to devise a method whereby solution could be kept in continuous passage through the soil substratum of the cultures so treated. A further treatment was added, by which the soil was kept near saturation all the time. This condition was quite comparable, in point of moisture content, to those cultures receiving the constant flow of solution. The treatment of each series is as shown in table on following page. In these studies all cultures were in the same type of vessels whether receiving aeration or the constant flow of solution through the substratum or not.

[1] Paper No. 144 of the Journal Series, New Jersey Agricultural Experiment Stations, Department of Soil Chemistry and Bacteriology.

[2] The kindly interest and helpful suggestions of Dr. J. G. Lipman and Dr. J. W. Shive in connection with this work are acknowledged with pleasure. The cultural work was carried out in the plant physiology laboratories.

SERIES NUMBER	CULTURE	TREATMENT
I	1 and 2	Simple soil cultures (60 per cent moisture)
II	3 and 4	With percolation and direct aeration
III	5 and 6	As I, with direct aeration alone
IV	7 and 8	Percolation alone
V	9 and 10	Simple soil cultures (90 per cent moisture)

Since the procedure involving the percolation of solution through a soil substratum in the presence of growing plants was found to be so readily carried out, it is thought that the possibilities of this method may extend much farther than its usefulness as a method of aeration. Since the volume of solution passed daily through the soil represents several times the normal amount of that contained in the soil, it is thought that this percolate represents the elusive soil solution to which the plant has access as faithfully as that obtained by any other method known. It would seem, therefore, that studies of its changes may indicate, in a reliable manner, the fundamental physical and chemical changes in the complex plant-soil solution system that are known to accompany plant growth.

It has been found possible to recover by this procedure unusually clear percolates, even from the heavy soil used in the present experiment, although at times, the reaction of the solution was almost neutral.

For the possible usefulness of the method in the study of the interphysicochemical relations of soil and plant, the procedure will be discussed in some detail before presenting the results of the study in aeration which the method first served.

METHODS

As a culture vessel which might receive a constant flow of solution through a soil substratum and at the same time support growing plants in a normal way, the type of container indicated in figure 1 was adopted. The preparation of the container has been described (2) as used for sand cultures. A large number of such vessels were prepared for these and subsequent studies by cementing together, after first removing the bottoms from all except the smallest, a series of three ordinary, coneshaped clay pots, the largest of which was about 14 cm. in the upper diameter and the smallest 7.5 cm. In cementing the pots together a fairly thin mixture of Portland cement was used. The bottom of the larger was fitted into the top of the smaller consecutively and the bottom of the smallest formed the bottom of the vessel thus constructed.

After thoroughly air-drying, the vessels were heated in a hot air sterilizer for the purpose of removing the hygroscopic moisture preparatory to treating them with hot paraffin both inside and outside while still warm. This treatment prevented loss of salts by impregnation in a fairly satisfactory manner. The opening through the bottom of each percolator was closed by a rubber stopper (*B*, fig. 1) carrying a short glass tube through which the percolating solution could escape. The upper end of this tube was loosely closed with a small plug of glass wool. In the soil work, a layer of clean sand sufficient to cover the glass wool was placed over this outlet.

The flow of solution into the culture (fig. 1) was controlled by using for the upper arm of the siphon a tube with a bore of $\frac{1}{2}$ mm. In this way about eighteen hours were required for

FIG. 1 TYPE AND CONSTRUCTION OF CULTURE VESSEL USED

emptying the bottle. The use of capillary tubing for this purpose has been previously described (2). The rate of flow necessarily decreased with the lowering of the level in the reservoir, but this was regarded as of no great importance since it was only desired that the total flow of one liter through the culture occur within twenty-four hours.

Instead of permitting the solution to drip directly upon the surface of the substratum as in the case of sand cultures, in work with soils a short tube was set upon a watch glass inverted just beneath the surface as indicated in figure 1. Inside the base of the tube a small amount of washed sand was added which sometimes was extended out to the edge of the watch glass as well and thus greatly facilitated percolation by constituting a sort of reservoir which offered a greater surface for diffusion outward and downward into the substratum.

It is to be noted that the lower arm of the siphon was constructed of tubing with an inside bore of 3–4 mm. and thus imposed no great resistance to the flow of the liquid. In the case of alkali soil studies where the rate of flow had to be much slower, the rate was further reduced by bending a loop in the capillary that extended nearly to the bottom of the bottle and thus the total length of that part was increased about two and one-half times.

Perhaps the greatest disadvantage that follows the use of this method in the case of soils is the high moisture content of the substratum which necessarily follows. However the aeration afforded by the practice of passing the solution through the culture daily has been found to correct this as a factor detrimental to plant growth, at least so far as the normality of the root and general development of the plant is concerned. This is indicated by the manner in which the root systems were found to fill the containers in those cultures so treated. In the later cultures with corn the roots were found to penetrate the entire soil mass so thoroughly as to grow out through the lower outlet at *B*. Excessive moisture in the vessel, which may occur particularly in the case of heavier types of soil, may be satisfactorily controlled by attaching a longer tube to the outlet at *B*.

STUDIES IN AERATION

Since factors pertaining to aeration of soils will usually be found to be of greatest concern in the heavier types, a heavy Elkton Silt Loam was used in the present study as outlined above. According to the Hilgard method, the maximum water-holding capacity of this soil was slightly in excess of 58 per cent. This type has been defined as consisting of a "grayish silt loam to a depth of about 10 inches which is loose and floury in well cultivated fields but tends to run together when wet and bake upon subsequent exposure." The subsoil is characterized by a grayish color somewhat darker than the surface soil and usually mottled. The type is of marine origin and is derived from deposits that have weathered under conditions of poor drainage.

It is worthy of note that but slight trouble was experienced so far as the permeability of the soil was concerned under the conditions described above to which it was submitted. The percolating solution was found to come through in an exceptionally clear condition throughout the period of the experiment.

Where direct aeration was used pressure was obtained from an improvised air pump previously described (1) and the air bubbled through a trap as shown

attached to the side of vessel 3 in plate 1, figure 2. From this trap the air was conducted to the lower part of the culture vessel and the tube turned upward at about the level of the lower joint, or about two and one-half inches from the bottom. From this point in the lower part of the soil mass a fairly rapid stream of air was passed upward through the substratum.

The vessels were of such size as to conveniently hold 2.6 kilograms of soil. After this amount of soil for each of the ten vessels was properly treated with acid phosphate and placed in the pots, sufficient salts (sodium nitrate and potassium sulfate) were added in the first liter of solution applied to make, in connection with the acid phosphate, the total fertilizer treatment equivalent to a 2000-pound application of a 5-5-5 mixture. Subsequent to this and daily throughout the entire period of the experiment the percolate received in the bottle below was made up to a liter and again passed through the culture. This procedure was thought to produce an aeration effect in the cultures comparable to that of the artificial cultures previously studied in solution and sand.

The number and arrangement of the cultures and the treatment of each series are given on page 98. The soil of the cultures receiving 90 per cent moisture, as indicated, was practically saturated all of the time. In the case of those receiving but 60 per cent moisture, the content was more nearly that regarded as optimum for plant growth. The soil of those cultures receiving the repeated flow of solution through the substrata was also found to be very near the saturation point for the greater part of the time. Barley seeds of a beardless variety were germinated and three uniform seedlings placed in each culture on October 2, 1922, and the growth period continued to December 5, in all, 64 days.

The results in terms of average relative dry weights are expressed graphically in figure 2 where relative values in grams are to be found at the foot of the respective columns. Perhaps an even better idea of the effects of the different treatments may be obtained from a study of the plants as shown in plate 1. In these the results of the different treatments are in decided contrast. It is seen that the culture with a high moisture content in the absence of aeration (plate 1, pot 9) gave a considerably lower yield than any of the other treatments. The simple cultures with a substratum having a more normal moisture content followed. The constant flow of solution through the soil of the cultures so treated was found instrumental in effecting a considerable increase in growth over those of the other treatments. But it is apparent that the application of direct aeration is the most effective of all, though there was only a slight difference between the effect of direct aeration alone and its combination with the repeated percolation of solution through the culture. This is quite the opposite of results found in the case of solution cultures discussed previously (2).

Only simple tests of changes in the hydrogen-ion concentration were made from time to time. The reaction of the percolate from cultures receiving the repeated flow of solution was determined at the intervals noted, and the soil

was tested at the time of harvesting the plants. For cultures not receiving the percolation treatment, the soil alone was tested at the intervals noted in the table.

The results of particular interest in these preliminary data on the change of reaction of the substratum as a result of plant growth are to be found not only in the progressive change of reaction of both the soil and the percolate, but in the marked difference in the extent of these changes. The change in reaction of the percolate was found to be considerably greater than in the soil mass. This may well raise an important question as to the nature of the changes which plant growth induces in its relation to the soil and the soil solution.

Culture No.	9 and 10	1 and 2	7 and 8	5 and 6	3 and 4
Treatment	90 per cent moisture	60 per cent moisture	Constant drip	Direct aeration	Aeration drip
Av. relative dry weight	100	150.5	193.0	219.5	221.2

FIG. 2. COMPARATIVE EFFECT OF AERATION AND CONSTANT DRIP UPON THE DEVELOPMENT (DRY WEIGHT) OF BARLEY T IN A HEAVY CLAY SOIL

It may be well to note, in this connection, that in his studies upon the liming of humus soils, Odén (6) studied the inverting power of these soils and concluded that this effect, according to the pH values, cannot be accounted for unless there is a concentration of hydrogen ions around the soil particle greater than that which expresses the reaction of the general mass of the soil. This may be considered in accord with the conclusions of van der Spek (7) when he notes the greater concentration of hydrogen ions that may be withdrawn to the soil particles from the soil solution than may be found remaining in the solution. He found them to be dislodged from their adsorbed condition by washing only with difficulty. In the presence of a rapidly growing crop,

therefore, this greater rate in the change in reaction of the soil solution towards neutrality under the conditions of salt application outlined, might be closely connected both with preferential assimilation of ions or radicals by the plant and the stability of the adsorption to the soil particles of those ions capable of properly counterbalancing this tendency.

Independent of these considerations, the fact which it was hoped to demonstrate by these experiments is the value to the respiratory processes of the plant of a sufficient supply of available oxygen to its roots. The data presented indicate that the response of barley to aeration in a heavy soil was decidedly positive and that any increase of compactness or imperviousness of the soil might well be considered as injurious to plant growth through the consequent decrease in the supply of available oxygen.

Although oxygen determinations were not made upon the percolates, it is of interest to note that in later experiments with a loam soil to which 25 per

TABLE 1

The hydrogen-ion concentration of the soil and percolate at different stages in the development of the barley plants

TIME OF SAMPLING	HYDROGEN-ION CONCENTRATION				
	Cultures 1 and 2	Cultures 3 and 4	Cultures 5 and 6	Cultures 7 and 8	Cultures 9 and 10
	pH	*pH*	*pH*	*pH*	*pH*
October 2 (2 days)	....	5.5*	....	5.45*	...
October 30 (4 weeks)	5.85	5.9*	6.1	6.15*	5.8
November 27 (8 weeks)	6.05	6.7*	6.25	6.7*	6.0
December 5 (harvest)	....	6.95*	....	6.95*	....
	6.1	6.0	6.0	6.1	6.3

* Value for percolating solution. All other values are for the soil of the respective cultures as determined in the usual way.

cent clay had been added, the comparative pressures of the gas in the solution of cropped and uncropped pots show that for the latter (fallow) pots the concentration of dissolved oxygen is as much as fourteen times as great as in the percolate of the cropped pots. This particular test was made in the evening after the percolate had flowed through the sampling bottle without coming into contact with the air for an entire day of bright sunshine. In further tests during the night, the differences in the oxygen pressures of the solutions were considerably less marked between the cropped and fallow soils. These studies were conducted during experiments involving the growth of popcorn under the same conditions of culture as those just described for the barley of Series IV in the present studies.

The procedure used in sampling for the determination of oxygen from such soil cultures is the result of an adaptation of the mikro-method of sampling already described (3). In doing this, the tube *b* of the sampling bottle (3, p. 490) is connected directly with the outlet tube of the percolator. With

the cock *c* open, the flow of the liquid will fill the bottle and pass out the arm *d*. In sampling in this manner, considerable difficulty has been experienced in avoiding the entrainment of bubbles of air which emerged from the culture vessel with the slightest exhaustion or evacuation of the system. A precaution that has been found helpful in overcoming this difficulty is to have the outlet *d* drop only to such a distance that instead of exerting a siphon effect, the opposite condition will prevail and, as a result, a slight pressure will develop in the system involving the arms *b* and *d*, the bottle *a* and the lower part of the percolator.

After a sufficient quantity of the liquid has passed through the sample bottle, the cock *c* is closed and the procedure in handling and treating the sample in preparing it for titration is the same as has been previously outlined (3).

REFERENCES

(1) ALLISON, R. V. 1922 The effect of aeration and continuous renewal of the nutrient solution, upon the growth of barley and buckwheat in artificial culture. *In* N. J. Agr. Exp. Sta. 43d Ann. Rpt., p. 409–413.

(2) ALLISON, R. V., AND SHIVE, J. W. 1923 Studies upon the relation of aeration and continuous renewal of the nutrient solution to the growth of soybeans in artificial culture. *In* Amer. Jour. Bot. (soon to appear).

(3) ALLISON, R. V., AND SHIVE, J. W. 1923 Micro-sampling for the determination of dissolved oxygen. *In* Soil Sci., v. 15, p. 489–491.

(4) HOWARD, A. 1922 Soil aeration in agriculture. *In* Agr. Res. Inst., Pusa, Bul. 61.

(5) LIPMAN, J. G., AND BLAIR, A. W. 1921 The influence of the mechanical composition of the soil on the availability of sodium nitrate and dried blood. *In* N. J. Agr. Exp. Sta. 42d Ann. Rpt., p. 303–316.

(6) ODÉN, SVEN 1920 The importance of liming humus soils. *In* Internat. Mitt. Bodenk., v. 9, p. 375–390.

(7) VAN DER SPEK, J. 1922 Action of neutral salts on soils. (Determination of soil acidity.) *In* Vers. Landbouwk, Onderz. Rijkslandbouwproefstat., p. 162–202.

FIG. 1. BARLEY IN HEAVY CLAY SOIL CULTURES

2. Simple culture (moisture 60 per cent)
6. Like 2 with direct aeration

FIG. 2. BARLEY IN HEAVY CLAY SOIL CULTURES

3. Constant drip with direct aeration
9. Not aerated (high moisture, 90 per cent)

THE STRATIGRAPHIC STUDY OF PEAT DEPOSITS[1,2]

ALFRED P. DACHNOWSKI

Bureau of Plant Industry, United States Department of Agriculture

Received for publication November 20, 1923

I. INTRODUCTION

The history and progress of peat investigations have been quite similar to the history and progress of other lines of scientific work. There are first the observations, many of them imperfectly made, then improvements in methods of work and a gradual accumulation of fundamental basic facts, finally the attempts to work out relationships for these facts. If the problems of peatland in the various states individually, or in the United States as a whole is to be solved permanently, and on the right basis, the facts as they exist must be the foundation of that solution.

During the past ten years the writer's primary object of peat investigations in the field has been first of all the collection and study of profile records of peat deposits, irrespective of the use made or the utility to be made of the peatland. The profile records of peat deposits have contributed the fundamental facts regarding the three principal groups of peat layers which, because of their immediate practical usefulness, are now occupying the interest of soil survey workers. The peat profiles brought out not only the natural units and divisions of peat materials included in the whole profile, but they have shown also the intrinsic characteristics of the horizons in the surface layers of drained peatlands upon which soil-forming processes have operated. Surface horizons in peat layers are very recent, practically being equivalent to the formation of muck and humus. The profile records, moreover, in their geographic relations have thrown a great deal of light upon the several kinds or groups of peat deposits, the series of type profiles in each group, and the conditions of their formation. These observations may conceivably lead at some future time to successful methods of selecting peatland. The profiles have brought out two important divisions of peat deposits; namely, (1) those which developed in water basins and under conditions of poor drainage and (2) those which developed on moist flat land under conditions of a

[1] Read by the author before the Chicago meeting of the American Association of Soil Survey Workers, November 14, 1923. Published by permission of the United States Secretary of Agriculture.

[2] This paper differs in character from those usually published in Soil Science. A special request for its publication has come from members of the American Association of Soil Survey Workers.—EDITOR.

rising or fluctuating water table. The type profiles in the former group of peat deposits show sedimentary layers of peat in the bottom and indicate the need of elaborate drainage measures for reclamation. The type profiles in the latter group of peatland exhibit as initial layers mainly fibrous or woody types of peat; deposits of this group can be readily drained and aerated to the bottom. There is another point in which profile records have been of immediate practical utility. Regarding the most important factors in the accumulation of peat layers, the profile records emphasize on the one hand the influence of the time interval during which various kinds of peat-forming vegetation contributed the number, character, and position of separate layers of plant remains; on the other hand they stress the significance of the limited supply of air. Consequent to the saturation with water, the decomposition of peat layers is prevented. Soil-forming processes can act only as the organic material becomes partially drained or cultivated.

These concepts relating to peat layers and horizons, to profile types of peat deposits, and to factors of peat accumulation have been presented in various publications (1–5). On the basis of these concepts a correlation of the experimental results has been made possible with reference to the profile structure of both American and European peatland. In their present genetic and geographic relationships these concepts are gaining acceptance among men active in field and laboratory peat investigations. Without reference to the practical importance to soil bacteriology and plant nutrition, knowledge of the profile section of peat deposits constitutes a distinct step forward for various lines of scientific work, including ecology, geography, economics, paleontology, and even archaeology. The stratigraphic section of a peat deposit,—the profile as a whole—must be the unit as well as the subject matter for a practical detailed survey, for the classification and mapping of peatland, and for questions of crop production. A consideration of the manner of occurrence, behavior, and adaptability of different layers of peat material at and beneath the surface is essential to the effective and intelligent conduct of agricultural and industrial operations. The location and construction of drainage channels, of roads and buildings on peat deposits, requires in advance information regarding the different layers of peat to be encountered. It is essential to test peat deposits with adequate sampling tools and with reference to layers and horizons, and to reconstruct with some degree of accuracy the main outlines of both surface and underground distribution of peat layers. In order to solve the problems arising from enforced practices such as excavating peat for the preparation of organic fertilizer composts, for sanding and flooding peat areas, or for finding the necessary means to meet undesirable field conditions which contribute to plant diseases, it is important to know and understand the stratification of peat deposits (6, 7). It is obvious also that the economic necessities with respect to qualified settlers and the country's future requirements of potential farmland require a better selection of peat deposits on the basis of structural quality.

Field work on peat deposits has now been effective over a sufficient time and area in this country to warrant the belief that an account of the method for the stratigraphic study of peat deposits may contribute to a better understanding of peat investigations as a field problem. Before proceeding, however, to a detailed description of the field method in use at this time it should be pointed out, in a brief summary, that the most important contribution from a stratigraphic field method consists in the recognition and description of the different layers of peat in the whole peat profile, their number and arrangement relative to one another, their thickness and continuity, the mineral subsoil, and the source of water supply.

In connection with these various criteria the separate horizons are established which have developed, in the surface of drained peatland, through the operation of soil forming processes such as aeration, cultivation, and others. In these cases, the effects and stages in disintegration and decomposition of the original plant material are also considered, and the thickness, texture, structure and color of each of these horizons in the upper part of the peat profile are determined.

The principle and method of differentiating peat deposits into series and type-profiles is based upon the number of peat layers and horizons, and upon a combination of characteristics rather than upon any single ecological, botanical, physical or chemical peculiarity. On the whole, the stratigraphic method of classifying and mapping peatland is essentially the same as that which is now being practiced for mineral soils. To determine the type profile and the proper boundaries of a peat area requires practice in clear visualization of the horizontal and vertical space relations of the different layers exhibited by peat deposits. Actual observations of the whole structure beneath the surface are impossible, however, except by means of soundings and test-holes, supplemented by observation in excavations and ditches. From the nature of things transitions and blending of peat layers cannot always be indicated in a profile record, or sharply drawn on the map; consequently indistinct peat profiles should be expected, making it impracticable, at least at present, to define certain peat areas, or to attempt to draw boundaries for them. Although certain peatlands, mapped under a given number, symbol or type profile by this method, may not always be closely similar to related deposits, yet a sufficiently complete knowledge and classification of that area is thus made possible. Unquestionably the stratigraphic method and its results will serve as a basis for further and better work.

II. CHARACTERISTICS OF THE DIFFERENT GROUPS OF PEAT MATERIAL

In order to identify in the peat profile the units or layers and horizons of organic material it is necessary to have a certain amount of botanical information regarding the plant remains which constitute peat. There are certain genetic relations between various kinds of peat, an elementary knowledge

TABLE 1

*Structural units of peat deposits and some of their physical characteristics**

GROUPS OF PEAT-FORMING VEGETATION	TYPES OF PEAT	CHARACTER OF PEAT LAYERS	COLOR OF PEAT LAYERS	TEXTURE OF PEAT LAYERS	STRUCTURE OF PEAT LAYERS
Aquatic	Macerated*	Pulpy (sedimentary)	Olive green, brown to black	Coarse to very finely divided	Compact, impervious, stiff, plastic or loose, friable
	Colloidal*				
Marsh	Reed*	Fibrous	Gray, red, or yellow-brown to dark brown	Coarse to fine fibered	Dense, matted, felty, or porous, spongy
	Sedge*				
	Brown moss*				
Bog	Bog moss*				
	Heath shrub	Woody	Dark brown to blackish brown	Coarsely fragmented to granular	Compact and granular, or loose, wicker-like
Swamp	Willow-alder shrub				
	Deciduous forest				
	Coniferous forest*				

* The characteristics and the physical appearance of the corresponding types of peat marked with an asterisk are among those shown in the illustrations on plates 1–5.

of which is essential to intelligent observation and interpretation. For this reason it may be of value to restate briefly the chief points of interest in the classification of the peat materials previously described (3) and to illustrate the character of some of the layers of peat (table 1 and plates 1–5).

For the convenience of the fieldman, the ten different kinds of peat now known, (their phases and variations run well into a hundred) may be placed into three chief groups; viz., the group of sedimentary layers of peat, the group of fibrous peat, and the group of woody layers of peat. This differentiation is basic and refers roughly to the preponderance of plant constituents and to textural, structural, and certain other characteristics. These features may be supplemented by quantitative measurements, such as water-holding capacity, diffusion of air and gases, conduction of heat, bacterial population, solubility of the organic material, etc. The importance of distinguishing between the three groups of peat layers can not be too strongly emphasized. A separation of this kind is necessary, since field observations have shown that differences in the profile of peat deposits are wide and important.

For general practical purposes, it is sufficient to describe peat materials occurring as layers in terms of composition, texture, structure, and color; this will give the necessary information to form a fairly good idea of the main differences between separate peat layers and to localize their relative position. For purposes of correlation it is desirable however, to classify peat layers more definitely by actually noting the botanical identity of the plant remains present. As potential soils they are not merely the physical support of growing crops; but they also furnish the energy and organic compounds which can be utilized either directly or indirectly by fungi and bacteria, and so be made available for higher plants. These and other peculiarities are very closely correlated to the botanical differences and character of the various layers of peat.

Pulpy peat layers

The most characteristic feature of pulpy peat layers is their sedimentary nature (plate 1 and fig. 2). Residual sediments are formed by the decay of aquatic vegetation; while transported organic sediments, derived from floating mats or various other units of vegetation, have been carried from their source of origin and redistributed usually by water currents, less commonly by wind. A layer of pulpy peat has no visible plane of bedding although the original sediments were laid down in practically horizontal position under conditions differing probably in rate of deposition, seasonal changes, and other causes. The plant remains are relatively small in size; in range of texture they vary from coarse to very finely divided particles, while in structure the layer may be impervious, dense, heavy, stiff and compact. When obtained moist the principal colors of the peat samples are black and dark brown or gray and olive green, with darker shades and variations upon exposure to the air. The material possesses the property of shrinkage to a remarkable degree; it becomes a very hard and hornlike substance upon

drying, and breaks with conchoidal fracture. Sedimentary layers of peat are easily excavated but do not stand in vertical walls. Under heavy loads and in ditches they yield gradually by plastic flow. Under conditions of good drainage pulpy peat has a tendency to break into angular fragments, finally weathering into a fine granular dust.

Pulpy, sedimentary, layers of peat invariably indicate conditions of accumulation below water; they may occur at, near, and below the surface of a peat deposit, in large masses or in comparatively small sheet like beds. The layers may be lenticular, gradually becoming thinner and giving place to overlapping layers of fibrous or woody kinds of peat. A sedimentary inclusion is therefore likely to resemble decomposed phases of surface layers of peat. A horizon of this kind, unless carefully examined microscopically, is often mistaken for the product of layers that are no longer protected by water from oxidation and decay. In penetrating layers of pulpy peat sheets of water may be found above them.

In the pulpy group of peat layers are included the macerated, colloidal, and doppleritic types of peat material. Transition phases may contain an admixture from fibrous or woody plant remains, or varying amounts of shells, chara marl, diatomaceous earth, and of mineral matter such as silt, sand, and clay.

Fibrous peat layers

The outstanding characteristic of fibrous layers of peat is their matted or felt-like porous nature, which has its origin in the interwoven network of more or less unaltered plant remains. The organic constituents are chiefly derived from roots, rootlets, and rhizomes of herbaceous plants and from mosses (plates 1–4 and fig. 2). Fibrous peat occurs in layers owing to the striking differences in the vegetation units themselves which have succeeded one another, and from which the separate units are derived. They differ widely in character. Their physical properties, ease of disintegration and decomposition, as well as various other features, are closely related to the botanical origin of the layers. Commonly the larger portion of a sample volume of fibrous peat consists of pore spaces; and as pores are continuous, layers of fibrous material are a medium in which water salts, or air may move freely. Because of this porosity, fibrous layers can be well drained and aerated and they stand up well in excavations and trenches. In texture, they vary from coarse to very finely fibered material, exhibiting on that account a rather loose, porous appearance. Pulpy peat when present as an admixture acts like a cement in a fibrous layer, making it firm and compact when dry. The colors are variable, ranging from shades of gray, red or yellow brown to dark brown. Contact with the air imparts a darker shade, and admixtures of finely divided organic matter add a very dark brown or black color; mineral salts may lend various shades of yellow, brown and red. Under conditions of slow drainage particles of finely fibered roots oxidize and disintegrate readily

into a black, granular material, but when overdrained they remain more or less unaltered and dry, owing to the high absorption of air.

The individual layers of fibrous peat may be very thin or they may be measured in feet, and accordingly may be described as thin bedded and thick bedded. Although laid down in practically horizontal position a layer of fibrous peat does not necessarily form a continuous stratum. It may occur interbedded or may grade into a layer of woody or of pulpy peat by admixture, or it may give place to overlapping beds of other kinds of fibrous peat material. It is not unusual to find fibrous layers which must be described by terms indicative of mixtures.

The group of fibrous peat layers embraces the "radicellate" reed and sedge types, and the moss types of peat; they are derived from well marked vegetation units which differentiate marshes and bogs.

Woody peat layers

The important feature of woody peat layers is the large amount of woody material from shrubs and trees either as the dominant component or as a prominent admixture in fibrous or finely divided peat material (plate 4, 5 and fig. 2). Owing to the lower water table required by peat-forming shrubs and trees, this group of peat layers is affected by aeration and weathering. The woody plant remains are broken down partly into granular debris and partly into irregular-shaped woody fragments which have escaped or resisted alteration by the decomposing action of air and microörganisms. The depth of the residual weathered debris, and the contact between the decomposing and the more or less unaltered woody material is liable to be extremely uneven, due to the rate of decay under local field conditions. On that account, layers of woody peat may show separate horizons, or an alternation of light brown and very dark brown or black granular organic material, giving the layer a banded or bedded appearance.

Woody peat layers differ widely in composition and character. Their texture, color, ease or difficulty of decay and other properties are more or less closely related to the nature of the plant remains. They may occur at various levels at and below the present surface of a peat deposit and may vary in thickness and continuity.

In the group of woody peat layers are included the types of peat derived from heath shrubs, from willow and alder shrubs, and from deciduous and coniferous forests.

Muck and humus

To the three characteristic groups of peat layers there should be added perhaps a fourth group to include muck and humus and those mineralized phases which are important members of the Clyde, Dunning, and other series of mineral soils containing a large percentage of organic matter. Much work is needed to supply the true facts concerning muck and humus, and

to determine their relation to soil problems. In the opinion of the writer both muck and humus represent approximately a measure of soil-forming processes to which drained surface layers of peat have been subjected. Muck and humus indicate stages of which the former is related to disintegration and the latter is the result of decomposition.

Disintegration is essentially a mechanical soil-forming process by which peat materials are broken into separate and smaller fragments of their constituent plant remains. In places a complete gradation may be seen from the very finely divided material that forms on a cultivated peat soil through various phases of disintegration to the well-preserved, unaltered layers of fibrous or woody peat below. The term disintegration means the physical breaking down of peat at or near the surface. Changes in moisture content, in temperature, more especially the action of freezing and thawing, the growth of plant roots, all play a part in this action. The conditions most favorable to disintegration of peat material are found on drained peat land that lacks the shading and protective covering of a surface vegetation. Peat layers when overdrained have more or less numerous natural partings owing to their irregular drying and shrinkage. The breaks, along which the organic materials separate readily, may be open cracks, or wide open crevices called fissures, and they may occur at intervals of a few inches or of several feet. Cracks and joints afford means of entry to air and soluble salts. Water freezing in cellular plant tissues will burst them causing thin fragments to break off from the parent material. Freezing water in a joint in planes between peat layers or in any crack or crevice exerts the same expansive force that it does in freezing in a pipe; the crack or joint is widened increasingly by each successive freezing and thawing and disintegration operates along and inward the numerous natural breaks. Where crops or native vegetation are growing the rootlets and roots of plants enter the pore spaces and capillaries in the peat material and gradually widen them.

The product of the disintegration of any peat layer is muck. Much of the organic material that has been termed muck is in fact merely the disintegrating drained portion of a peat deposit of which the surface material is in a mechanically divided condition. It may contain varying amount of mineral matter, but the nature and condition of the organic material can be readily determined with the microscope. The sizes of plant fragments may vary in range from the large angular, lumpy pieces of woody debris to the very finely divided particles suspended in the water of the brown, coffee-colored streams of some peat lands. Woody and fibrous peat layers contain more or less abundant fragments of the plant remains that have not been completely broken down. Pulpy, sedimentary layers of peat, on the other hand are less subject to disintegration, since they are themselves on the whole the transported products of disintegration of former water plants or a floating mat of marsh plants, or other vegetation units growing along the shores of water bodies.

Decomposition is a collective term. It includes on the one hand the alterations which plant remains undergo as a source of energy within the drained and aerated or cultivated surface layers of a peatland; and on the other hand it involves the separation from the resistant material of those constituents which are soluble and may nourish crops. The process varies greatly, depending on the position of the ground-water level below the surface. Water soaked layers of peat undergo a very slow partial decomposition because of insufficient oxidation. When a peat layer is drained the plant remains are no longer protected by water from decay and much of the peat material is converted into carbon dioxide. Owing to the loss of the organic matter decomposition produces a great shrinkage of the layer and a proportional increase in the percentage of mineral matter. All peat materials at or near the surface of a drained peat deposit are attacked more or less rapidly by the destructive action of air, changes in temperature and other agencies. The attack on the peat materials is, therefore, mechanical, chemical and biological as well. These three processes are all active, but in any one place a single type of decay may be relatively predominant, owing to the kind of peat material and the field conditions under which the material is decomposed. In every instance, however, some of the more resistant organic constituents are merely broken into smaller fragments (disintegrated); others are changed in their nature (decomposed); while soluble portions remain or go into solution and are carried away. No peat material however resistant can long withstand the normal destructive processes of decay. In decomposition the active agents are air and microörganisms. They destroy peat layers by altering biochemically the constituent plant remains, producing new substances which on the whole are softer, darker in color, and finer in texture than the original parent material. Decomposition is accelerated by factors which are within the control of man; it is favored by manuring and tillage, by warmth and conditions of moderate moisture content. Low temperatures, dry air, or water containing no oxygen have little or no effect on altering and dissolving the organic matter of a peat layer. The field conditions relative to decomposition should on that account be carefully examined. Fluctuations in the water table, the application of lime, fertilizers and manures, methods of cultivation,—these have a very vital relation not only in the formation of surface horizons, but also to the microörganic life of the surface peat soil, and consequently upon the feeding conditions of future crops.

Oxidation produces a very noticeable change in the color of peat materials, and this coloration is one of the most obvious signs of initial decomposition. Peat layers which are submerged in water are usually of lighter color owing to the withdrawal of oxygen from the organic material.

The products of decomposition are commonly referred to as humus. Some of the products are a very dark colored, more or less resistant carbonized, earthy mixture of organic material, the characteristics of which can no longer be recognized microscopically, or based on those of the former parent layer of

peat. Other humus products are soluble; they may be taken into solution by water and used by growing plants, and they may become deposited underground or at the margin of a peat deposit. The organic material of hardpans is thus deposited as cementing material in the pore spaces of sand or silt, which they traverse. Fissures, joints, and crevices in dry peat layers frequently are filled by dissolved organic material which is precipitated from solution. A considerable part of the "doppleritic" veins and the filling of cracks and fissures in peat layers with crystals of mineral salts, deposited from solutions by water, is formed in this manner.

Humified layers of peat may be stained or their color may be changed by infiltration of suspended or dissolved organic matter, and by compounds of iron, sulfur, lime or other mineral salts. Horizons that contain considerable amounts of calcium sulfate crystals, oxidized iron, or an admixture of mineral matter washed in from uplands become proportionally more earthy upon the decomposition and loss of the organic matter. In humid regions in which the action of weathering consists of a progressive leaching of soluble material from the decomposing surface layer of peat and no carbonate is being accumulated, the humus may become distinctly acid and remain raw, resistant organic debris. Sandy subsoils develop a strongly marked gray layer, followed by a brown or yellow iron-stained horizin. In less humid areas, which differ widely in both climate and weathering, the surface layer may show horizons of humus, followed by muck over layers of peat. There is near the surface, in a definite position in the profile, an increasing accumulation of lime and other salts from ground waters, regardless of the amount existing in the original peat material or in the mineral soils below and adjoining the deposit. Leaching processes become more marked again in peat deposits of the southern coastal states where the rainfall is greater. Since humus as well as muck are a feature which has been acquired after an accumulation of peat was drained, the quantity of humus has no reference to the relative age of a peat deposit.

III. EXAMINATION OF PEAT DEPOSITS

In the conduct of a profile examination of peat deposits it is important to supply fieldmen, unfamiliar in the nature of peat investigations, with some from of field sheet for recording observations, and with published maps of the area. Time and energy can thus be conserved and the efficiency increased without loss to accuracy of detail or freedom of investigation. The form of field sheet which has been used by the writer more recently is shown in table 2. Where topographic sheets or soil maps do not exist, the fieldmen have the additional task of constructing one. This can be done, however, in the manner detailed for other surveys.

For the proper understanding of the agencies through which the several layers of peat have accumulated, careful attention is necessary to the general

TABLE 2

UNITED STATES DEPARTMENT OF AGRICULTURE

PEAT INVESTIGATION RECORD

Tally Sheet No.....State.....County.....
Location of peat deposit: Twp.....R.....Sect.....
Name and address of owner.....
.....Name of peat deposit.....
Location of profile section: Line.....Sta.....Field No.....Lab. No.....
.....
By.....For.....Date.....

1. *Topography*.....
.....Elevation.....
Acreage: Total.....% Used.....
% Primitive.....% Forested.....
Depth: Max.....Min.....
2. *Vegetation:* Native.....
Dominants.....Density.....
.....Associates.....
4. *Drainage conditions*.....
Water Table.....inches above surface
below
Color of water.....
Salt content.....
Sources of water supply.....
Depth of ditches or tiles.....
Distance apart.....
5. *Mineral Subsoil*.....
Character.....Color.....
Injurious substances.....
Soils adjacent to deposit.....
Geology of area.....
6. *Climatic Conditions*.....
Date of drought.....Frost.....
Unusual weather.....
Length of growing season.....
7. *Crop Record with best yields*.....
.....
Crops of poor yield.....
Weeds.....
Plant Diseases.....
.....
.....
8. *Industrial use of peat deposit*.....
.....
.....
.....
.....
9. *Prehistoric relics*.....
.....
.....
.....
10. *Remarks*.....
.....
.....
.....
.....
.....

3. *Description of profile section,* (Character, color, texture, structure of peat layer; water level, mineral subsoil).

0	
1	
2	
3	
4	
5	
6	
7	
8	
9	
10	
11	
12	
13	
14	
15	
16	
17	
18	
19	
20	

physiographic features of the area to be examined. Information as to whether the area represents the general features of a river valley, a terrace, an ancient glacial lake bed, an outwash plain, or a pocket in a morainal belt has a suggestive value of no small importance. A knowledge of the geology and soils of the region, the character of crops and of the native vegetation, and the nature of the water supply should be obtained beforehand to prevent errors.

The chief reason for the study and mapping of peat deposits is the occurrence, in the profile, of layers of peat tangible and definite enough so that these can be located and identified in the field. The examination consists essentially of plotting on a section map the location, distance and direction of profile soundings. To measure distances a simple odometer is generally preferred, while direction may be determined by means of a compass or a regulation sketching case.

The location of the more important profile soundings in a foot traverse should be indicated on the base map by a square mark; that of testholes by a round mark. Soundings for a detailed profile should be located by the fieldmen with reference to roads, bridges, houses, section lines or natural features shown upon the base map. Judgment must be exercised as to the number and the distance between the intermediate testborings necessary in any given area to establish changes in the character of the profile or the mineral subsoil. The necessity for detailed soundings depends upon the relative complexity of the peatland area. In a locality of obviously uniform topographic history profile soundings may be widely scattered. A change in the native vegetation or topography may indicate to the experienced field men the places and conditions which should be tested or verified by a profile. Points thus established should be sketched at once in the field as the examination progresses. For each day a tracing of the sectional peat map should be made complete in every detail with profile, legends, symbols, lettering and scale. It should be attached to the form sheet with notes, photographs or other records taken at the respective time. This procedure will aid in verifying any disagreements as to peat materials, or relating to other matters encountered in the field traverse.

In the work of identifying the botanical composition and physical character of the different layers in the profile of a peat deposit, it is necessary to examine the area from the surface downward through the entire vertical section. As a rule these examinations can be made with a peat sampler of the type illustrated in plate 5, figures 2 and 3. This instrument is a brass tube, provided with a brass plunger and with extra couplings of steel rods each two feet long, so that it can be extended to any desired depth. Augers and similar instruments of the type of a boring tool are unworkable in most peat deposits, and they introduce the serious difficulty of inaccurate measurements owing to the tearing of the fibrous or woody sample which is obtained with them.

To ascertain the variations in the profile, and the character of the different horizons and layers of peat and the mineral subsoil, it is necessary to sound

one foot at the time. Otherwise important changes at definite depths may be overlooked. Marked variations in color, texture, structure and degree of disintegration, the occurrence of fungi in their vegetative form, the presence of hard pan, thin seams of marl, silt, clay or of peat material charred by previous fires, should be examined and noted with some detail. In some cases the contact or separation layer between peat and mineral subsoil is clearly marked. In other cases, however, the texture of the peat in the presence of a considerable amount of inorganic matter makes a distinction between the two difficult to see.

The examination by means of soundings should include also the position of water pockets in or between layers of peat. The presence of sulfuretted hydrogen is usually indicated by the odor of the peat sample and the discoloration of the brass portion of the sampling instrument. According to recent information hydrogen sulfide is undesirable in peat deposits as it corrodes drainage pipes. In such instances attention should be given to any marked physical differences in the peat materials, and in the mottling or chemical and mineralogical features of the inorganic subsoil. The occurrence of highly ferruginous material, either distributed throughout the profile or in the form of concretions, near the margin of the peat deposit, or on its surface, should also be noted. The presence of unusual amounts of vivianite, crystals of gypsum, iron pyrite, or the occurrence of incrustations in ditches and on surface soils, and any excess of soluble salts in the supply of ground-water should be examined and confirmed by laboratory methods whenever possible. Marked acid or alkaline conditions may be tested by means of standardized litmus papers, or other indicators.

It is advisable also to inspect open drains or to dig a few holes in the ground. It is easier to obtain with a spade or large knife a smooth, vertically-cut surface, which can be observed without disturbing the layers of peat. It will generally be observed that in some localities the color, texture, and stratification may change often fairly abruptly. There is a further advantage from observing open ditches or digging a hole, in that the experienced fieldman can see the nature of the effects of drainage or of the mineral subsoil upon the surface horizons in the profile. Moreover, the actual appearance of the undisturbed layers of peat may often reveal quite as much regarding the suitability of the area for certain crops or other uses, as a subsequent more laborious method of laboratory analyses.

The recognition of peat profiles and the description and identification of layers of peat on the basis of their character and arrangement constitutes, no doubt, the most important contribution that can be made by a stratigraphic study of peatland. Great care should, therefore, be exercised in the identification and collection of peat samples in order that they may be representative of their respective area and actually represent the layers and different types of peat. A peat material to be correlated with a type should conform in certain general features to the descriptions of peat materials referred to

before (3). The illustrations of peat materials in natural size (plates 1–5), are presented for purposes of aiding those who desire information on the general appearance of some of the usual types of peat material encountered in profiles. Variations or phases will occur at different depths or in different localities but such differences do not greatly affect their grouping. New or doubtful kinds of peat should be placed into one of the respective general, main groups of woody, fibrous, or pulpy peat, and receive a name accordingly.

The texture and structure of a peat layer are determined partly by the different admixtures and proportions of different sizes of plant remains, in part by the arrangement of the components. Some peat materials obtained in soundings from below the surface may appear unaltered and perfectly fresh; but they soon darken in color and break down rapidly on exposure to air. Occasionally an apparently unaltered peat material will begin to go to pieces after exposure for a few days or longer. Field description and structural evidence on that account are more decisive than that obtained in the laboratory. Observations in the field should not be limited to specific samples but cover a large range of variations. In this manner gradations may be traced from obscure to identifiable forms and thereby the changes peculiar to the given locality may be recognized. Alterations in dry peat samples are often extensive and varied and hence may become unsafe guides unless the local variations are known from field observations. Under conditions of over drainage very finely divided plastic colloidal peat hardens and breaks into angular fragments, in contrast to the fine textured granular product from disintegrating fibrous and woody peat layers.

In the selection of samples of peat for laboratory examination at least one representative sample for every layer or type of peat recognized in the area should be secured. If a mixture of surface material is desired small samples should be obtained from twelve to sixteen different places at some distance apart but all from the same area and layer of peat. Samples from subsurface layers and from mineral subsoils should be secured in six to ten test-borings, without mixing or contamination in any way. Each of this series of samples should be packed separately into a cloth bag, glass bottle or paraffined paper box for shipment to the laboratory.

Variations in peat materials comprising a considerable range in character, texture, or structure should be recorded in the note book, and so described that they may be included in the final report. Where a good vertical section can be obtained from ditches or dug holes it will be advisable to separate the profile into a series of brick shaped sections, and to label and pack each separately. The location of samples and other material collected in the progress of the examination, should be carefully noted in the field book. The profile soundings from which samples are taken and submitted for further study should be indicated on the base map with a serial number.

For possible extensive laboratory or greenhouse work samples from various depths or localities should be taken in adequate amounts; they should be

collected during the progress of the field work, rather than at the completion of the survey. It is frequently impossible to collect at a later period on account of unfavorable weather conditions or lack of time.

The tags attached to field samples of peat should have the field serial number and should indicate the location of the place from which the material was obtained, its depth, the date, name of the collector, and remarks if neces-

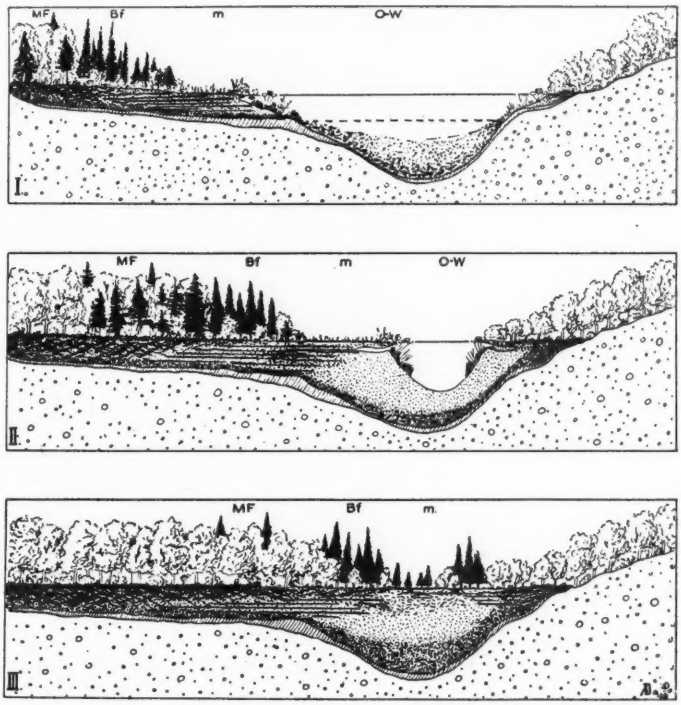


FIG. 1. GRAPHIC PRESENTATION OF THE DEVELOPMENT OF A PEAT DEPOSIT

The diagrammatic profile illustrates also the character, location, and continuity of different layers of peat.

sary, concerning the examination desired. This information should be written in ink or indelible pencil, and it should be in general accord with the more detailed description given in the field sheet.

After the observed facts relative to the several profile soundings are assembled certain inferences can be made as to the surface conditions in peat areas lying between points of actual observation. Similar inferences can also be drawn as to the conditions beneath the surface and expressed in vertical diagrams; the cross sections should represent the profile that would be exposed by making a vertical cut down through the entire peat deposit

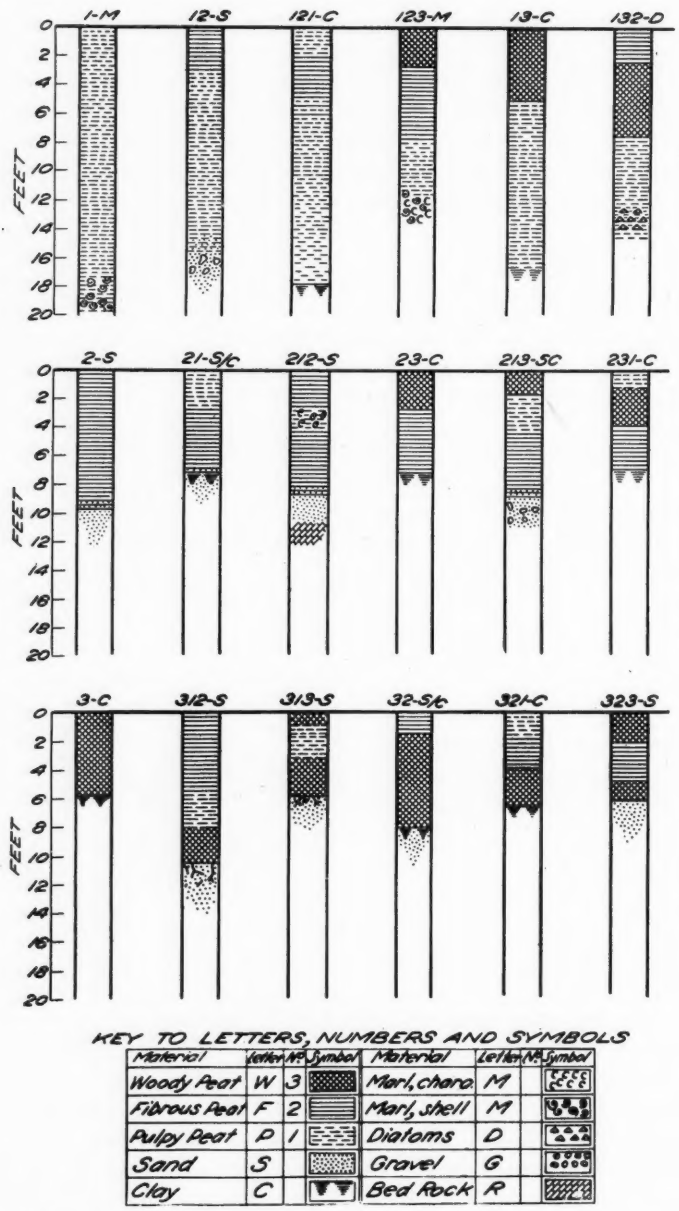


FIG. 2. GENERALIZED CROSS-SECTIONS TO SHOW SERIES OF THE MORE COMMON TYPE PROFILES IN THE TWO GROUPS OF WATER-LAID AND LAND-LAID PEAT DEPOSITS

along certain selected lines (fig. 1). Diagrams of profile sections are a great aid to a thorough comprehension of the conditions of a peat deposit along a line of traverse; they visualize the space and time relations represented by a peat area. Differences in peat layers and peat profiles should be shown graphically by the use of certain symbol-patterns inserted in the text. In figure 2 are shown the conventional letters and symbols employed to represent respectively the character and thickness of the several peat layers, and the nature of the mineral subsoil in the profile. Horizons and layers which are not sharply defined in the profile of a deposit are indicated by a merging of boundary lines.

A peat map is a graphic illustration of all available information assembled in proper relations, pertaining to the surface and the stratigraphic features of peat deposits in a given locality. A peat map should show, therefore, not only the boundary lines between different type profiles in so far as is clearly warranted by observed facts, but also the whole thickness of each deposit. The following colors to represent differences in depth of peat accumulation are suggested: a light brown color for shallow peat deposits varying from eight inches up to three feet in depth; a dark brown color for peat areas of greater depth than three feet. Differences in type profiles and their characteristics should be indicated by means of numbers or some other conventional designation. Cartography and graphic methods have made considerable advance in foreign countries, notably the Scandinavian countries, Russia, and Germany.

In figure 2 is shown a series of the more common type profiles in each group of peat deposits encountered in field work. The numbers used to express these units of mapping are combinations based on the group number of the respective peat layers in the profile, beginning at the bottom of the section. In these numbers the first and last numeral deserve special attention: the former implies the original position of the water table, and hence the extent to which the peat area can be drained; while the latter numeral denotes the surface peat layer which is or will be influenced by soil forming processes. A great many sub-types may be recognized upon the basis of differences in thickness, texture and structure of layers, and in surface horizons of disintegrating organic material in drained peat areas, but all have the generalized profiles as stated. Profile numbers may be shown on the completed map as overprints together with the symbol pattern indicating the nature of the mineral subsoil.

The writer believes that the field methods here outlined will make it possible not only to determine the actual extent and location of peatland resources, but also to take up relationships to the practical utilization of selected peat areas for crops, pasture, reforestation, wild life reserves or other purposes. The method is offered as an aid toward furthering peat investigations, farming practices and state and national peatland policies.

REFERENCES

(1) DACHNOWSKI, A. P. 1912 Peat Deposits of Ohio. Geol. Survey Bul., s. 4, Bul. 16, (In coöperation with U. S. Bureau of Mines.)

(2) DACHNOWSKI, A. P. 1916 Agricultural possibilities of Ohio peat soils. *In* Jour. Amer. Peat Soc., v. 9, p. 10–21.

(3) DACHNOWSKI, A. P. 1919 Quality and value of important types of peat material. U. S. Dept. Agr. Bur. Plant Indus. Bul. 802.

(4) DACHNOWSKI, A. P. 1920 Peat deposits in the United States and their classification. *In* Soil Sci., v. 10, p. 453–464.

(5) DACHNOWSKI, A. P. 1921 Correlation of time units and climatic changes in peat deposits of the United States and Europe. *In* Proc. Nat. Acad. Sci., v. 8, p. 225–231.

(6) DACHNOWSKI, A. P. 1922 Preparation of peat composts. U. S. Dept. Agr. Bur. Plant Indus. Cir. 252.

(7) DACHNOWSKI, A. P. 1923. Contribution of peat investigations to the cranberry grower. *In* Jour. Amer. Peat Soc., v. 16, p. 96–106.

PLATE 1

FIG. 1. Brown, compact, plastic, coarsely divided, pulpy peat of sedimentary origin. Natural size.

FIG. 2. Finely divided colloidal peat which hardened and cracked upon drying; it possesses conchoidal fracture and breaks into angular fragments. Natural size.

FIG. 3. Brown, coarsely divided, pulpy peat with an admixture of fibrous plant remains from reeds. Natural size.

FIG. 4. Surface view of black, friable, pulpy peat with shells. Natural size.

FIG. 5. Gray brown pulpy peat with portions of reed plants infiltrated with iron—Surface view. Natural size.

FIG. 6. Surface view of brown Hypnum peat. Natural size.

FIG. 7. Black, friable, sedimentary peat with marl from shells—Side view. Natural size.

FIG. 8. Dark brown, sedimentary peat containing nodular concretions of iron—Side view. Natural size.

FIG. 9. Brown finely fibered Hypnum peat on gray silt—Side view, showing well-marked line of separation between organic material and mineral subsoil. Natural size.

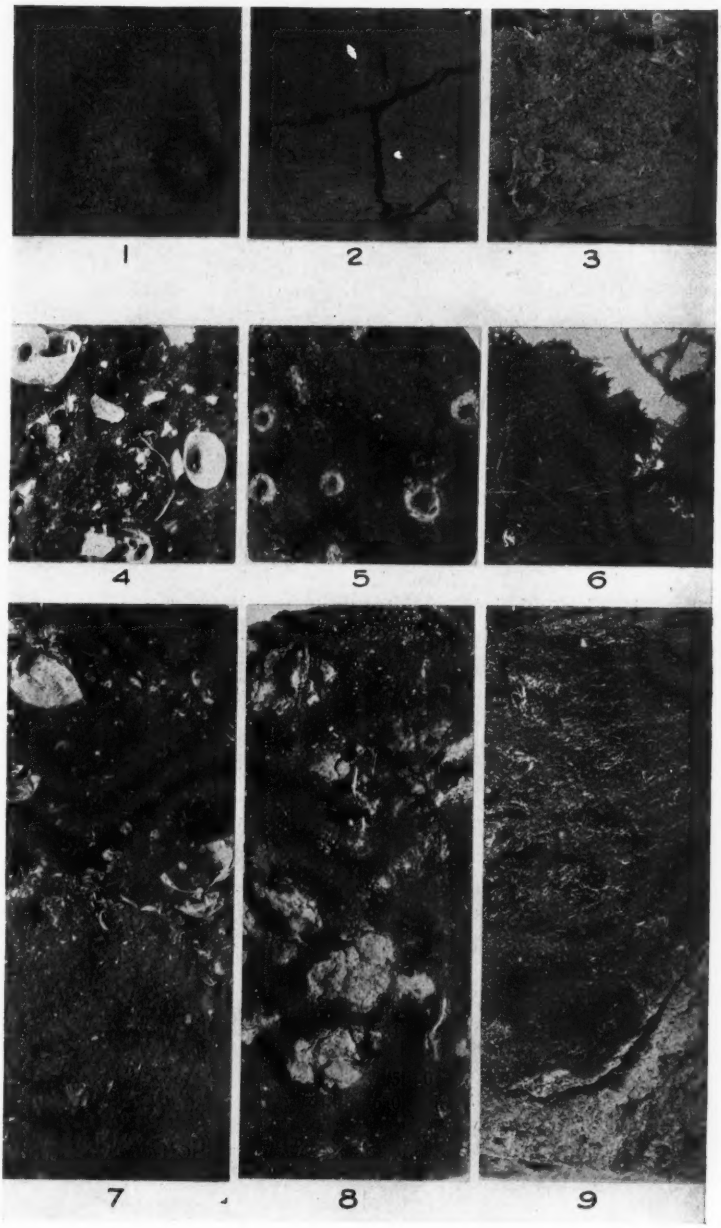
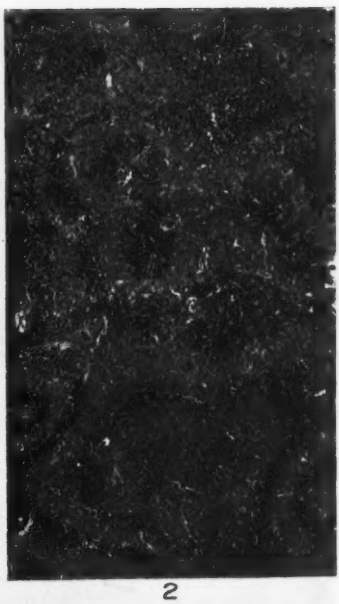

1
2
3
4
5
6
7
8
9

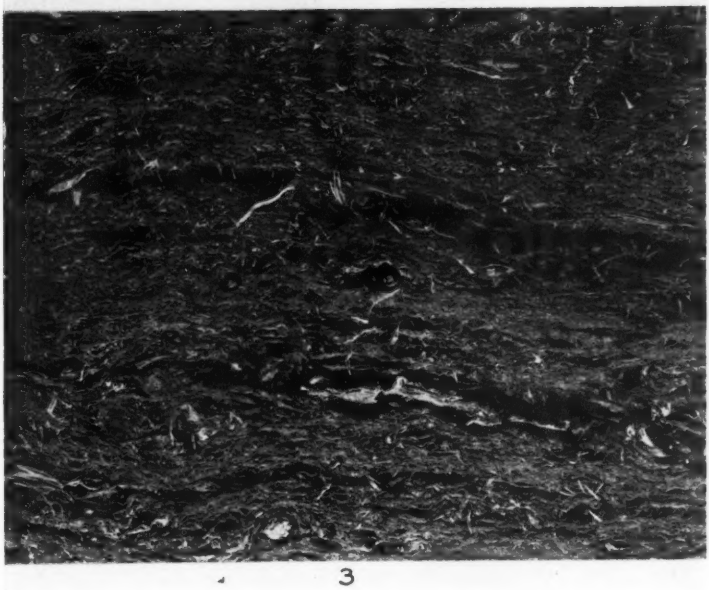
PLATE 2

FIG. 1. Light brown, coarse, fibrous reed peat. Natural size.
FIG. 2. Dark brown, finely-fibered, felty sedge peat. Natural size.
FIG. 3. Brown, porous, matted coarsely-fibered reed peat. Natural size.

1



2



3

PLATE 3

FIG. 1. Brown, loose, coarsely fibered sedge peat—Cross section of a layer floating as a mat near the margin of a pond. Natural size.

FIG. 2. Gray-brown, loose coarsely fibered sphagnum peat—Side view of a section cut from a surface layer. Natural size.

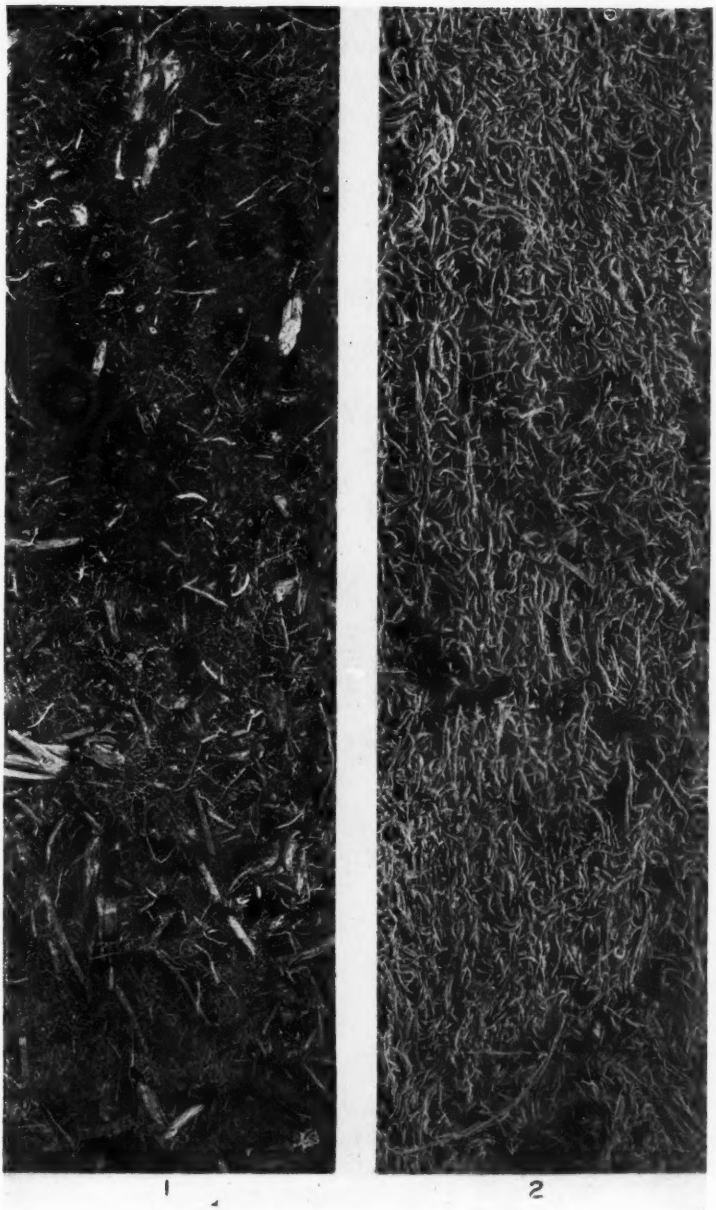

1
2

PLATE 4

Gray-brown fibrous sphagnum peat resting on a layer of finely-fibered, dark brown, compact sedge peat; the woody material in the horizons at *a* and *b* is derived from heath shrubs growing as a surface vegetation—Side view of a cross section cut from the surface. Natural size.

a
b

PLATE 5

FIG. 1. Dark brown, loose, forest peat containing varying amounts of coarsely fragmented woody material, root fibers, and well disintegrated granular debris—Side view of a cross section cut from the surface layer. Natural size.

FIG. 2. Brass instrument used for profile soundings of peat deposits. One-half natural size.

FIG. 3. Brass plunger, withdrawn from the brass cylinder to show spring with catch which locks the instrument at any desired depth. The cylinder, when filled with peat, protects the sample from any contamination with other material.

1
2
3

EFFECT OF IGNITION AT VARIOUS TEMPERATURES UPON CERTAIN PHYSICAL PROPERTIES OF SOILS

GEORGE JOHN BOUYOUCOS

Michigan Agricultural Experiment Station

Received for publication November 19, 1923

INTRODUCTION

It is generally known that igniting mineral soils to very high temperatures produces very marked change in their physical condition which in turn affects greatly their physical properties such as texture, structure, plasticity, absorption, water-holding capacity, etc. This change is particularly noticeable in the colloidal types of soil. Very little, however, is known regarding the degree of change of these properties at various temperatures of ignition, and especially the particular temperature at which the change commences to take place.

In connection with studies on soil temperatures that are being conducted by this laboratory it appeared very desirable and important to make a study of the degree of change brought about in soils by igniting them at different degrees of temperature. As a measure of this change three distinctly different properties were chosen for comparative study; viz., heat of wetting, unfree water and plasticity. These three properties were studied for each soil at several degrees of ignition from quite low to very high. It was thought originally that the results obtained from these studies would not only be of interest in showing the initial temperature at which the change commences and the degree of change that takes place at the various temperatures of ignition but also that they might probably suggest or furnish the much needed method of estimating the colloidal content of soils.

METHOD AND PROCEDURE

For igniting the soils an electric furnace was employed. The temperature of this furnace was measured by means of a couple which was standardized and was accurate to within 10°C. Four different degrees of temperature were finally adopted for igniting the soils. These are 110°, 230°, 485°, and 800°C. The furnace was kept regulated so that these temperatures remained quite constant. The soils were heated at these various temperatures for a period of about seven hours. After they had cooled, their heat of wetting, unfree water and plasticity were studied. The heat of wetting was measured according to the method described in former publication (1). It consisted of placing 50 gm. of air-dry soil in a wide glass tube and allowing it to dry in an electrically heated oven at a temperature of 110°C. for 24 hours. The tube was taken out, closed with a rubber stopper and allowed to attain the room temperature. After the exact weight and temperature were ascertained, the soil was quickly

and carefully poured into a calorimeter containing 100 grams of water, and the heat of wetting was ascertained. Extreme care was taken before mixing to have both the soil and water at exactly the same temperature and very nearly that of the room temperature. In order to be able to convert, if necessary, the rise of temperature into heat calories, the water equivalent of the calorimeter was determined. This was found to be 25 gm. For the specific heat of soils, the value of 0.200 was employed for the mineral soils and 0.300 for the organic soils unburned. For the burned organic soils, the same value was used as in the case of the mineral soils.

The unfree water was measured by means of the dilatometer method, already described (1). The moisture content employed was at the proportion of 20 gm. of soil to 15 cc. of water. Before the final measurement was made the soils were subjected to freezing and thawing once or twice. The soils were then placed at a temperature of 1.5°C. and allowed to come to equilibrium and the volume on the dilatometer stem recorded. They were then immersed at a temperature of about 12°C. for about fifteen minutes, and then returned to the original temperature. After equilibrium was attained the volume on the dilatometer stem was again read and from the two readings the unfree water could be calculated. The term unfree water is used in this paper to designate the soil water remaining unfrozen at the temperature of slightly below zero. All the water which freezes very readily or at very near zero is designated as free water. The free water is beyond the direct influences of the soil and consequently is not at liberty to freeze as the free water.

In the case of the plasticity measurements, unfortunately there is no scientific method and recourse had to be made to the old finger-test. Although no accurate measurements can be made by such a method, by practice one can learn to estimate and compare the plasticity of the soils fairly well, and it is believed that in the present study, a measurable change in the plasticity of soils as influenced by the various degrees of ignition could be detected.

EXPERIMENTAL

In table 1 are presented the results on heat of wetting and in table 2 the data on unfree water.

Examining first table 1 some very interesting facts are revealed. In the first place it is at once seen that the igniting of soils tends to decrease the property of heat of wetting. But this decrease does not become appreciable until rather high temperatures of ignition are reached. At the temperature of 230°C.[2] for instance, the decrease amounts to only about 5 per cent for many soils, taking the temperature of 110°C. as a standard which is generally used for drying soils. In some soils the decrease amounts to more than 5 per cent but this is true mainly in soils which contain considerable amount of organic matter, such as the Iowa Carrington clay loams. On the other hand some other soils such as the Minnesota black surf which also is rich in organic matter does not show very much change and in the case of the peats and mucks there is an actual increase instead of a decrease in the heat of wetting. This increase is apparent even at the ignition temperature of 485°C. These results of the peats and mucks are contrary to those of the mineral soils and the possible explanation for them may be that many of the organic particles are resistant to wetting and also they are so hard that water penetrates into them with exceedingly slow rate and great difficulty. The higher temperatures probably helps to destroy that resistance to wetting and also cracks the hard particles, with the result that more surface is wetted at the

higher temperatures of heating than at the low and consequently more heat is given off.

The intermediate temperature of 170°C. was also tried but the results obtained showed that in many of the soils the heat of wetting was practically the same as that at 110°C. Hence this intermediate temperature was abandoned in favor of that at 230°C., which may be considered as the temperature at which a measurable change in physical condition of the soil commences to take place.

TABLE 1

Effect of ignition on the heat of wetting of soils

Rise of temperature caused by 50 gm. of soil in 125 gm. of water

SOILS	HEAT OF WETTING			
	Ignited at 110°C.	Ignited at 230°C.	Ignited at 485°C.	Ignited at 800°C.
	°C.	°C.	°C.	°C.
Penn silt loam	0.90	0.80	0.50	0.0
Ohio silt loam	0.80	0.70	0.35	0.0
Michigan clay loam	2.10	2.00	1.85	0.0
Iowa Carrington clay loam	3.40	2.85	1.20	0.0
Minnesota black surf	2.85	2.70	0.65	0.0
Illinois clay loam	3.50	2.95	1.45	0.0
Michigan clay	1.65	1.40	0.75	0.0
Illinois red clay	3.50	3.20	1.60	0.0
Wisconsin Superior clay	1.95	1.40	0.95	0.0
California Merced clay	4.00	3 80	1.70	0.0
Upper Michigan clay	2.05	1.90	1.00	0.0
Muck	8.6	11.50	10.00	0.0
Peat	10.50	13.00	11.50	0.0
Fullers earth	8.00			0.0
Ferric hydroxide	3.75			0.0
Silica gell	9.60			0.0
Aluminum hydroxide	8.35			2.4

The data in table 1 further showed that at the ignition temperature of 485°C. the heat of wetting of all the soils except the peat and muck, has been considerably reduced, but it is still quite appreciable, in most of the soils, the decrease being less than 60 per cent of the original. This comparatively small decrease is very significant in showing that the physical constitution and properties of the soils which give rise to the heat of wetting are very resistant and are not destroyed or radically altered even at as high temperature as 485°C.

On the other hand the same table shows that as soon as the ignition temperature of 800°C. is reached, the properties of the soil which give rise to the heat of wetting are totally and completely destroyed and the property of heat of wetting completely disappears. This is true of all the soils, both inorganic and organic, the only exception being that of aluminum hydroxide

which still gives heat of wetting at the highest temperature due probably to hydration. Outside of the last material, all the soils and other artificial materials failed to give any heat of wetting whatever when they were ignited at the temperature of 800°C.

These results are not only interesting *per se* but they are also very significant in suggesting the possibility that a method might be evolved for estimating the colloidal condition or content of soils and the degree of activation. There is no doubt, of course, that the material which gives rise to the phenomena of heat of wetting is the colloids of the soil and their degree of activation. Since this phenomenon of heat of wetting completely disappears upon ignition at a certain temperature it logically follows that the colloidal content or state is completely destroyed by the heat at that temperature. That such is the

TABLE 2

Effect of ignition on unfree water in soils

SOILS	UNFREE WATER IN SOILS			
	Ignited at 110°C.	Ignited at 230°C.	Ignited at 485°C.	Ignited ot 800°C.
	per cent	*per cent*	*per cent*	*per cent*
Penn silt loam	7.5	7.0	6.5	0.0
Ohio silt loam	3.5	3.3	2.8	0.0
Michigan clay loam	13.6	12.0	9.5	0.1
Iowa Carrington clay loam	16.5	13.7	12.0	0.0
Minnesota black surf	14.0		2.75	0.0
Illinois clay loam	16.0	15.5	10.5	0.6
Michigan clay	10.2	11.0	8.5	0.0
Illinois red clay	17.2	18.0	16.0	3.0
Wisconsin Superior clay	16.5	13.7	10.8	2.7
California Merced clay	21.2	19.8	16.2	2.0
Upper Michigan clay	16.4	15.0	14.0	2.1

case appears to be proved by the fact that upon grinding the burned soils including the most colloidal clays, to as fine condition as it is possible to grind them and then determining again their heat of wetting, it is found that they lack this property just as before grinding. That this property of soils can be completely destroyed by ignition irrespective of the resulting fineness of particles is further shown by the data on ashes of mucks and peats. The ashes of these materials of course are extremely fine and yet they give no heat of wetting. These results are important and significant.

From these general data on the effect of ignition on the heat of wetting, a method appears to be suggested for estimating the colloidal state or content of soils and their degree of activation. This problem is now under extensive investigation.

Considering next table 2 it is also seen that ignition tends to decrease the unfree water in soils. The amount of unfree water is greatest in the unburned

soils, then becomes smaller with the increased temperature of ignition and becomes exceedingly small or entirely disappears when the soil has been heated at 800°C. These results correspond and agree with those on the heat of wetting.

The effect of ignition on plasticity was studied on several heavy clays including Michigan clay, California Merced clay, California Stockton clay, Illinois clay loam, Illinois red clay, Nebraska Pierre clay and Decatur clay. The results obtained show that when these soils were heated at 230°C. the plasticity in all cases was, as far as could be ascertained, the same as before heating. Heating them to 485°C. the plasticity, in all cases, disappeared almost completely in the original structure, but was greatly restored by grinding them. Heating them to 800°C. the plasticity in all of these disappeared completely both before and after grinding.

These results, therefore, agree with those on heat of wetting and unfree water, and they all go to show that these three properties are affected by heating in the same way, i.e., they begin to be affected at the same initial temperature and they are completely destroyed at the same degree of temperature.

SUMMARY

An investigation was conducted to study the effect of heating of soils at various temperatures upon the degree of change that takes place in the soils and the temperature at which the change commences, and ends. Three physical properties of the soils were chosen upon which to study this change, namely, heat of wetting, unfree water and plasticity.

It was found that all these three properties begin to be affected at about the same initial temperature which is about 230°C. At this temperature a change in these properties just commences to be perceptible.

At the temperature of 485° all three properties are greatly reduced, but they are not as yet entirely destroyed. At the temperature of 800°C., however, they become entirely destroyed and completely disappear.

When soils are heated to 800°C. no matter how fine they are ground again they give no heat of wetting. Even ashes of peats and mucks give no heat of wetting, even though they are so exceedingly fine. These results strongly suggest the possibility of evolving a method of determining or estimating the colloidal content or condition of soils, and their degree of activation.

REFERENCES

(1) Bouyoucos, George J. 1917 Classification and measurement of different forms of water in the soil by means of the dilatometer method. Mich. Agr. Exp. Sta. Tech. Bul. 36.

(2) Bouyoucos, George J. 1918 Relationship between the unfree water and the heat of wetting of soils and its significance. Mich. Agr. Exp. Sta. Bul. 42.

MICROBIOLOGICAL ANALYSIS OF SOIL AS AN INDEX OF SOIL FERTILITY: VII. CARBON DIOXIDE EVOLUTION[1]

SELMAN A. WAKSMAN AND ROBERT L. STARKEY

New Jersey Agricultural Experiment Stations

Received for publication, December 12, 1923

HISTORICAL

The evolution of carbon dioxide has been used by a number of investigators as an index of the decomposition of organic matter in the soil.

Wollny (38) found in 1880 that the carbon dioxide content of the soil rises and falls with the amount of organic matter present in the soil. Kiszling and Fleischer (8) used the production of carbon dioxide in peat soils as an index of the rapidity of the decomposition going on in the soil; the addition of sand was found to stimulate oxidation, while the temperature was among the most important factors affecting oxidation.

Déhérain and Démoussy (2) placed the soil under examination in a closed tube of 100 cc. capacity and kept it at constant temperature. At the end of a certain period of incubation, the gas was extracted and the carbon dioxide present determined. It was found that the formation of carbon dioxide was due almost entirely to the action of microörganisms and that the carbon dioxide content increased with temperature to about 65°C., then decreased, and at 90° another increase took place due to chemical agencies. There is an optimum moisture content for the formation of carbon dioxide, which is also influenced by the state of division of the soil and its aeration. Although sterile soils were found to produce small amounts of carbon dioxide, the latter increased twenty-five times when soil infusion was added [Severin (23)]. Sterilized and inoculated soil gave two to five times as much carbon dioxide as unsterilized and uninoculated soil.

Russell (21) measured the actual amount of oxygen absorbed by the soil as an index of soil oxidation instead of determining the carbon dioxide produced. He found that the rate of absorption of oxygen increased with temperature, the amount of water (up to a certain point) and the amount of calcium carbonate present in the soil. These conditions also increase soil fertility. Russell, therefore, suggested the use of soil oxidation as a measure of fertility. The amount of oxygen absorbed measures the total action of soil microörganisms, which are responsible for the decomposition processes in the soil.

Stoklasa and Ernest (30) placed 1-kgm. portions of sieved soil in glass cylinders through which a current of air was passed at the rate of ten liters in twenty-four hours. They observed that the evolution of carbon dioxide by a soil, under certain conditions of moisture and temperature, in a certain length of time, can furnish a reliable and accurate method for the determination of bacterial activities in the soil; the presence of organic matter and the temperature were found to be of greatest importance. Stoklasa (25, 26) further found that the evolution of carbon dioxide occurs most abundantly in neutral or slightly alkaline soils, abundantly supplied with readily assimilable plant nutrients and well aerated.

The production of carbon dioxide [Stoklasa (27)] was in direct proportion, not to the total carbon content of the soil, but to the available organic matter in the soil. The evolution of

[1]Paper No. 152 of the Journal Series, New Jersey Agricultural Experiment Stations, Department of Soil Chemistry and Bacteriology.

carbon dioxide was thus found to be an index of the availability of the soil organic matter, or the ease with which it decomposes. Two methods were suggested by Stoklasa (27, 28, 29) to demonstrate this; (1) the determination of the amount of carbon dioxide produced in twenty-four hours by 1 kgm. of soil remoistened after first being air-dried and (2) sterilizing the soil and then inoculating 1 kgm. with 10 gm. of cattle manure extract and determining the amount of carbon dioxide produced in twenty-four hours. The two methods gave the following results:

SOIL TYPE	CARBON CONTENT	CO_2 PRODUCED IN 24 HOURS BY 1 KGM. OF FRESH SOIL	CO_2 PRODUCED IN 24 HOURS BY 1 KGM. OF STERILIZED, INOCULATED SOIL
	per cent	*mgm.*	*mgm.*
Tenacious clay soil	1.68	8.2	14.0
Diluvial loam	2.12	14.6	27.8
Alluvial soil	1.73	36.6	59.8

The amount of carbon dioxide produced was found to depend on the quantity and kind of organic matter, physical and chemical condition of the soil, numbers and kinds of microörganisms. It was found to serve as an index not only of the activities of the microörganisms of the soil but of the amount of readily decomposable organic matter.

Carbon dioxide evolution was thus found to run parallel with numbers of microörganisms and also [Stoklasa (27)] with nitrification in the soil, as shown in the following table:

SOIL DEPTH	UNCULTIVATED, UNFERTILIZED LOAM SOIL		CULTIVATED, FERTILIZED, UNDER CLOVER		MANURED AND FERTILIZED, CULTIVATED UNDER BEETS	
	Bacteria in 1 gm.	CO_2 by 1 kgm. in 24 hours	Bacteria in 1 gm.	CO_2 by 1 kgm. in 24 hours	Bacteria in 1 gm.	CO_2 by 1 kgm. in 24 hours
cm.	*thousands*	*mgm.*	*thousands*	*mgm.*	*thousands*	*mgm.*
10–20	230	16.5	1,800	38.6	4,700	47.5
20–30	256	19.4	2,350	38.8	3,529	49.7
30–50	208	9.8	1,600	20.2	2,100	28.5
50–80	14	3.3	540	6.3	184	6.6
80–100	5	2.1	72	2.7	95	2.3

Van Suchtelen (32) passed a current of air, usually 16 liters in 24 hours, through 6 kgm. of soil placed upon pure sand in a jar. The intensity of carbon dioxide production was found to be much greater at the beginning of the experiment and rapidly decreased after a short while. The amount of carbon dioxide produced was measured until it reached a uniformly low level; the average amounts of carbon dioxide produced per unit time from the different soils served for comparison. He concluded that the determination of carbon dioxide formation by different soils furnishes a better means for estimating the bacterial activities in the soils than the numbers of bacteria. Cultivation, aeration and nutritive salts were found to exert stimulating effects upon carbon dioxide production; moisture and organic matter content of the soil are among the most important factors. In a later contribution, van Suchtelen (33) considered the microbiological activities in the soil from the standpoint of energy. The amount of heat produced by a given soil under laboratory conditions, during a definite interval of time, was taken as a unit of comparison.

Rahn (20) used sugar solutions containing $CaCO_3$ and inoculated with soil; he measured not only the carbon dioxide produced by the microörganisms from the sugar but also that formed from the interaction of organic acids with $CaCO_3$. The use of carbon dioxide production in soil as a measure of soil fertility was also suggested by König, Hasenbäumer and Glenk (11), who measured the carbon dioxide evolved from 1 kgm of soil with and without the addition of 1 gm. of glucose or urea.

Russell and Appleyard (22) found the curves for bacterial numbers, nitrate and carbon dioxide content of the soil air sufficiently similar to justify the view that all these phenomena are related. A rise in bacterial numbers was accompanied by a rise in the carbon dioxide content in the soil air and somewhat later by a rise of nitrate in the soil. The rate of decomposition of organic matter in the soil was, therefore, looked upon as a function of bacterial activity. The rate of biochemical activities in the soil was found to attain maxima in late spring and in autumn, and minima in summer and winter. In autumn the bacteria increased first, then the carbon dioxide content rose, and finally the nitrate increased.

Most of the early work and considerable later work on carbon dioxide in soils has been carried out with the gases taken from the soils *in situ*. A large amount of such work seems to demonstrate the difficulties of obtaining indicative results by analyzing the atmosphere of field soils in place.

Pettenkofer (18) suggested a method for measuring the carbon dioxide produced by soils. He aerated soils with carbon dioxide free air through a container and measured the carbon dioxide in the outgoing air.

Petersen used a similar apparatus (17) and since then the Pettenkofer method has been used extensively by numerous investigators with various modifications. Among these might be mentioned Wollny (39) who aerated the soil mixed with sand, Déhérain and Démoussy (2) Stoklasa and Ernest (30), van Suchtelen (32), Lemmermann, et al. (13), Klein (9), and Gainey (6).

Russell (21), and Darbishire and Russell (1) used oxygen consumption, to measure soil oxidation processes. Leather (12) extracted the gases from the soil samples by suction and subsequently analyzed them for carbon dioxide.

Few of these methods have been used to any extent recently. The method commonly used at present is to measure the carbon dioxide in air, previously freed from carbon dioxide, passed continuously over the surface of soil placed in containers. Under these conditions the soil more nearly approaches normal conditions than where it is aerated, which greatly accelerates microbiological activities. This method has been used by Fred and Hart (5), Fraps (4). Potter and Snyder (19), Merkle (14), Neller (15) and has proved satisfactory in our hands.

Potter and Snyder (19) state that the amount of air passing over the soil in the laboratory does not materially affect the amount of carbon dioxide evolved. The addition of moisture to an air-dry soil was found to result in a rapid increase in the amount of carbon dioxide evolved, followed by a gradual drop. Previous drying of the soil alters its colloidal condition, permitting an increased rate of oxidation. It also alters the chemical condition of the organic matter making it more readily available for the activities of microörganisms. Similar results were obtained by Klein (9) and others.

Neller (16) determined the carbon dioxide producing capacity of the soil by placing tumblers containing 200-gm. portions of soil, to which 0.75 gm. of soybean hay had been added, under bell jars, through which carbon dioxide free air was passed for sixteen days. On comparing two limed and two unlimed soils, he obtained distinct correlations between crop yield, nitrate accumulating and numbers of bacteria, but these did not correlate with ammonia accumulation, as shown below:

PLOT NUMBER	CROP YIELD (10 YEARS)	CO_2 PRODUCTION	NO_3-N* ACCUMULATION	NH_3-N* ACCUMULATION	BACTERIAL NUMBERS
	lbs.	*mgm.*	*mgm.*	*mgm.*	*millions*
11A (acid)	2282.4	353.4	10.3	11.93	2.5
11B (limed)	2928.0	505.6	22.3	11.44	6.2
21 (acid)	2015.8	389.9	16.1	11.56	5.1
24 (limed)	2661.1	542.0	33.9	11.68	6.5

* From 100 mgm. nitrogen in the form of dried blood.

König and Hasenbäumer (10) also found that carbon dioxide formation goes hand in hand with bacterial numbers. Gainey (6) observed the parallel formation of carbon dioxide, ammonia and nitrate from organic substances rich in nitrogen (cottonseed meal and dried blood), when moisture and aeration were favorable; the correlation was especially noticeable between the ammonia and carbon dioxide production.

The discrepancy between Neller's and Gainey's results can be readily explained by a consideration of the carbon and nitrogen metabolism of the microörganisms concerned, especially the fungi. It will be shown elsewhere that the relative amounts of carbon dioxide and ammonia formation from any organic substance depends upon the metabolism of the particular organism and the carbon-nitrogen ratio of the organic material. For every unit of carbon assimilated by the organism, as well as for the carbon dioxide formed, there is a definite amount of nitrogen assimilated. When the organic matter (dried blood or cottonseed meal) contains more nitrogen than the organism needs for metabolic processes, a part of the nitrogen will be left as a waste product in the form of ammonia; when the organic matter contains less nitrogen than the organism requires, there will be no ammonia accumulation and the carbon compound will be decomposed only so far as the nitrogen supply, whether present in the material or added in inorganic forms, will permit.

Gainey determined the carbon dioxide formation and ammonia accumulation from nitrogen-rich organic materials, such as dried blood or cottonseed meal. It would be expected that both would run parallel, since for every unit of carbon used up, either for structural or energy purposes, there is a corresponding amount of nitrogen liberated, as ammonia, in excess of that required by the organism. Neller, however, determined carbon dioxide production from soybean meal, a substance comparatively low in nitrogen, and ammonia formation from dried blood. The rate of decomposition of these two substances in the same soil, as indicated by the evolution of carbon dioxide, is different, as shown by Starkey (24).

It is also important to point out that the formation of carbon dioxide in the soil depends not only upon the absolute carbon content of the soil, but upon the ease of its decomposition, as shown by Stoklasa (27) and Gehring (7).

A brief review of the literature, therefore, tends to indicate that the evolution of carbon dioxide is a good index of decomposition of organic matter, of microbial activities and of soil fertility. The fact that the numbers of microörganisms and the nitrifying capacity of soil have been found in previous investigations (34, 36), to be good indices of soil productivity and the fact that Stoklasa (28, 29), Russell and Appleyard (22), Neller (15), van Suchtelen (32) and others found that evolution of carbon dioxide runs parallel to bacterial numbers and to the nitrifying capacity of the soil, tend to emphasize further that we are dealing here with an important soil microbiological process, which may serve as a proper index for a microbiological analysis of the soil.

METHODS

In studying the power of the soil to decompose organic matter, we often use the terms "oxidative capacity," "carbon dioxide producing capacity," "capacity for decomposing organic matter," "respiratory capacity of soils," etc., all of which mean about the same, namely the decomposition of organic matter in the soil by microörganisms, whereby energy is liberated. Carbon dioxide may be formed not only as a result of oxidation, but as a result of hydrolysis, as in the case of formation of alcohol and carbon dioxide from dextrose.

$$C_6H_{12}O_6 = 2C_2H_5OH + 2CO_2$$

On the other hand, energy may be liberated without the formation of carbon dioxide, as in the case of the anaerobic transformation of dextrose to lactic or acetic acids.

$$C_6H_{12}O_6 = 2CH_3CHOH \cdot COOH \ (+ \ 15 \text{ Cal.})$$
$$C_6H_{12}O_6 = 3CH_3 \cdot COOH \ (+34 \text{ Cal.})$$

Some carbon dioxide undoubtedly also originates in normal soils from carbonates interacting with organic or mineral acids by biological agencies.

The absorption of oxygen would also be only a partial index of energy transformation, since some energy is liberated without the intervention of free oxygen. It would, therefore, be more accurate to use the calorific value of the soil, or liberation of heat as a result of the activities of microörganisms, as an index of energy transformation, as suggested by van Suchtelen (33). However, in view of the complex apparatus necessary for the determination of the latter and in view of the fact that the carbon dioxide is a final product of energy utilization by the majority of heterotrophic soil microörganisms, while only a small amount of it is reassimilated by the autotrophic bacteria, we may use the evolution of carbon dioxide as an index of respiration of soil microörganisms without danger of introducing appreciable errors.

A differentiation should be made between the "respiratory power of the soil" itself and the "decomposing power of the soil" or its ability to decompose added organic matter. Respiratory power is measured by the carbon dioxide produced (from the soil itself), when a definite amount of soil is placed under optimum conditions of moisture and temperature. This depends upon:

1. The number and kind of microörganisms present. 2. The amount of organic matter in the soil. 3. The composition of this organic matter (the degree of its decomposition). 4. Soil aeration. 5. Moisture content. 6. Physical condition of the soil. 7. Chemical composition (altered by fertilization). 8. Soil reaction. 9. Kinds of plants grown (Stoklasa, 25).

Decomposing power is measured by the rate at which a soil decomposes organic matter added to it. It is influenced by most of the factors mentioned above, particularly by the microbial population and the physical and chemical conditions of the soil. Furthermore, a difference in the composition of the organic matter used will effect a change in the activity of the various groups of soil microörganisms and different soil constituents may become limiting factors, e.g., nitrogen or phosphorus, if the added organic matter is low in these.

The amount of carbon dioxide produced in sterilized soils inoculated with a strong cellulose-decomposing organism, preferably a rapidly growing fungus may also be measured. This is preferable to the use of manure, as done by Stoklasa, since no additional nutrients are added with a pure culture.

The "respiratory power of the soil," which indicates the condition of the organic matter in the soil, its ease of decomposition or its availability, when the soil is brought under favorable temperature and moisture conditions, as

well as activities of microörganisms in the given soil or their respiration intensity can be determined in three different ways:

1. One-kilogram portions of fresh soil, from a composite sample taken to a depth of 6½ inches and put through a 3-mm. sieve, are placed in pots. Enough water is then added to bring the moisture content of the soil to the optimum. The pots of soil are then placed in the respirator and the amount of carbon dioxide evolved determined at various intervals for seven to fourteen days. This method has been used in our investigations.

2. One-kilogram portions of air-dried, sieved soil, taken to a definite depth, are placed in proper containers, adding the necessary amount of water, and the carbon dioxide evolved in forty-eight hours is determined. Stoklasa (28, 29), using only a twenty-four hour period, found that an infertile soil, poor in organic matter, will produce 8–14 mgm. carbon dioxide, a good beet soil produces 56–68 mgm., and a medium soil about 30 mgm.

3. One-hundred gram portions of fresh soil, prepared as for method 1, are placed in 300-cc. flasks with long necks (*A* in fig. 1). Cotton plugs are placed in the necks of the flasks and in the glass connections. After the proper amount of water is added (50 per cent of total moisture-holding capacity), the flasks are sterilized for 1–1½ hours, on two consecutive days, at 15 pounds pressure. The soils are then inoculated with a culture of a common green *Trichoderma* which was found to be one of the most active groups of soil fungi decomposing celluloses, proteins, pectins and other complex organic substances. The flasks are then connected with the $Ba(OH)_2$ tubes in the respirator and the amount of carbon dioxide evolved is determined for 12–14 days. This method has not been used extensively in the following experiments, but the results obtained are very indicative. Two soils, 5A a fertile soil rich in organic matter, and 7A an infertile soil, poor in organic matter were compared. By this method, 124.08 mgm. and 37.40 mgm. of carbon dioxide respectively were found to be given off in eight days.

The "decomposing power of the soil" can be determined by a group of methods, which differ chiefly in the kind of organic matter added to the soil. A few substances are suggested here, since their decomposition is directly influenced not only by the microbiological activities in the soil, but also by its chemical composition, the presence of available nitrogenous substances and to a lesser extent of phosphates.

1. *Dextrose.* This substance is very readily decomposed in the soil and an excess of material as well as a long period of incubation may obliterate finer differences in the activities of the microörganisms in the different soils. Five hundred milligrams of dextrose was added to 100 gm. of soil. The carbon dioxide evolved was determined every six or twelve hours for a period of 48–72 hours and curves were obtained, which bring out distinctly the differences in the microbiological activities of the different soils. Since dextrose is used very readily as a source of energy not only by the soil fungi and actinomycetes, but also by the great majority of heterotrophic soil bacteria, including the nitrogen-fixing organisms, the rate of decomposition is very rapid. The utilization, by the soil organisms, of all the nitrogen available, during the decomposition of dextrose, will not necessarily stop the production of carbon dioxide. If the nitrogen-fixing organisms are at all active in the soil, they will tend to obtain nitrogen from the atmosphere. In case these organisms fail to develop rapidly and the small amount of nitrogen available is used up, the depressing effect of the limited amount of nitrogen will be registered in the decrease in carbon dioxide production.

2. *Cellulose.* The carbon dioxide evolved from 1 gm. of cellulose added to 100 gm. of soil gives information not only on the "decomposing power of the soil" but also on the amount of available nitrogen and phosphate present in the soil. This is due to the fact that the cellu-

lose is decomposed in the soil (with the exception of alkaline or partially sterilized soils) primarily by fungi. These rapidly growing organisms consume a great deal of nitrogen in the synthesis of their mycelium and it soon becomes a limiting factor. The whole question of cellulose decomposition in the soil will be discussed in detail in the following paper of this series. The distinctive difference in the curves of carbon dioxide evolution from dextrose and cellulose has been pointed out by Dvořák (3).

3. *Rye straw and alfalfa meal.* One per cent of alfalfa meal has been used extensively in our studies as reported below. Ordinarily 200 gm. portions of soil were incubated with the organic matter for a period of fourteen days. Rye straw contains about 0.5 per cent of nitrogen and alfalfa meal about 2.5–3.0 per cent, hence the available nitrogen in the soil may become a limiting factor in the first case, but probably will not in the second.

4. *Dried blood.* The use of one per cent of dried blood or other organic material rich in nitrogen, such as casein, permits the determination of the "protein-decomposing" capacity of the different soils. Measurement of ammonia accumulation was not found to be a reliable index of decomposition of organic matter for reasons pointed out elsewhere (35). Ammonia

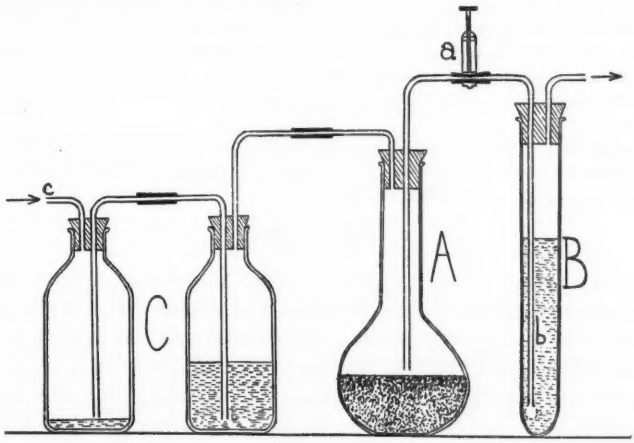


FIG. 1. SMALL APPARATUS FOR DETERMINING THE DECOMPOSING POWER OF SOILS

is an intermediate product in the nitrogen metabolism of a number of organisms and a waste product in the energy metabolism with proteins as a source of energy. It is, therefore, subject to various changes. Carbon dioxide, however, is a final product in the energy utilization. That the rates of ammonia and carbon dioxide formation from proteins are very similar is shown by Gainey (6).

APPARATUS

The apparatus which was used to determine the carbon dioxide evolved from the soils in most of the work was not essentially different from that described by Neller (15, 16). The pots of soil were sealed under bell-jars with paraffin. Air, freed from carbon dioxide by passage through soda lime and through bottles of 10 per cent sulfuric acid, was then drawn through the bell-jars. From there the air was drawn through a modified Truog absorption tower (31) containing 50 cc. standard 0.25 *N* barium hydroxide. The stream of air was drawn through the apparatus continuously at the rate of three liters per hour for the duration of the experiment except for the intervals when the solutions were titrated.

The source of the suction was a water pump described by Neller (15) which gave a steady uniform suction. The apparatus consisted of two sections: one of six and one of seven units. The excess barium hydroxide was titrated back periodically with 0.25 *N* oxalic acid to determine the carbon dioxide absorbed, using phenolphthalein as an indicator. The towers were then renewed. One unit of the apparatus was always blank and was used as a control on the appara tus. Any neutralization of the $Ba(OH)_2$ in the tower connected with this unit was considered to be due to the manipulation and at each titration period allowances were made for this control on all titrations of the $Ba(OH)_2$ from the units containing soils. Ordinarily only very slight corrections were necessary. Six differently treated soils were run in duplicate at one time.

A smaller apparatus was devised for determining the decomposing power of soils. Part of one unit is illustrated in figure 1. The long-neck, flat-bottom flask *A* of 300-cc. capacity took the place of the respiration chamber which in the apparatus described was a bell-jar mounted on a wooden base. The Truog absorption tower was replaced by the 100-cc. test tube *B*. The bulb at the end of tubing *b* was perforated with numerous small holes to break up the bubbles of gas. The air, freed from carbon dioxide by passage through soda lime, was distributed to the various units at *c* and then entered the traps *C*, containing 10 per cent sulfuric acid. This solution prevented diffusion of the gas from one unit to another. The tubing in the two bottles is so arranged as to keep the solution in the traps in the event of back pressure. The air passed over the soil in the respiration chamber and then through the solution in *B* which absorbed the carbon dioxide. From *B* the tubing led to the constant-level siphon water pump.

The respiration apparatus in all cases was enclosed in an incubator room at 25–28°C. The smaller apparatus is less cumbersome than the other and many more units can be run without occupying as much space as the large apparatus.

SOILS USED

Plots of soil from the nitrogen series which have been fertilized alike for fifteen years and used in the previous studies of microbiological methods have also been used in these experiments. A careful record has been kept of the fertilizer applied to the various soils and the resulting crop yields. Although the numbers of microörganisms and nitrifrying capacity of the same soils has been reported previously, the results obtained at the time of sampling for the study of evolution of carbon dioxide are also reported here in order to have a basis for comparison. Ten to twenty-five samples were composited from each plot and put through a 3-mm. sieve.

For the main series of experiments, 1-kgm. portions were placed in glazed earthenware pots of 1-liter capacity. Enough water was added to bring the moisture to optimum which was 50 per cent of the total moisture-holding capacity. To test the decomposing power of the soil, 1 gm. of alfalfa meal was thoroughly incorporated with 200 gm. of soil and enclosed under the belljar respirators in tumblers. The carbon dioxide production from soils treated as in these two cases was determined for 14-day periods.

In determining the production of carbon dioxide by means of the small apparatus, 100-gm. of soil was placed in the flask *A* and 500 mgm. of dextrose was added in solution and well mixed into the soil. The amount of solution added was sufficient to bring the soil moisture content to optimum. When dextrose was used the production of carbon dioxide was measured at six-hour or twelve-hour intervals for 48–72 hours.

With the large apparatus only duplicate determinations were made with each soil. It was found, however, that the results checked up very well. When some organic matter (alfalfa meal) was added for the study of the decomposing power of the soil, discrepancies were often obtained between duplicate determinations, due probably to the uneven distribution of the added material. The simplified apparatus will permit the making of more than 2 determinations for each soil.

Results

The treatment of the plots, crop yields,[2] nitrfying capacity and numbers of microörganisms are given in table 6. The results on the respiratory power of the soil and on the decomposition of alfalfa meal and dextrose are given in tables 1–5.

The annual fertilizer applications per acre made to the soils used in these experiments are as follows:

PLOT NUMBER	FERTILIZER TREATMENT
5A,* 5B	Minerals,† 16 tons cow manure
6A	Minerals, 16 tons horse manure
7A, 7B	Untreated
9A	Minerals, 320 pounds $NaNO_3$
11A, 11B	Minerals, $(NH_4)_2SO_4$ equivalent to 320 pounds of $NaNO_3$
19A	Minerals only

* The plots marked A are unlimed; those marked B receive two tons of ground limestone every 5 years.

† Minerals = 640 pounds acid phosphate and 320 pounds of muriate of potash per acre.

The results on the respiratory power of the soil as determined by our own method, namely from one kilogram of fresh sieved soil, brought to optimum moisture and incubated for fourteen days, are given in table 1. The respiratory power of the soil, by the same method, but only during the first forty-eight hours of incubation is given in table 2. The results presented in table 2 are comparable with those of Stoklasa, who allowed the soil to air-dry, then added moisture and determined the evolution of carbon dioxide in twenty-four hours. In our experiments, fresh sieved soil was used, since it was found that air-drying produces decided physical, chemical and biological changes in the soil. A two-day period of incubation is preferable since twenty-four hours may not be, in some cases, sufficient to free the chamber from all the carbon dioxide.

The results obtained from the two- and fourteen-day periods of incubation are quite comparable. The manured soils (5A, 6A, 5B) lead by far in the

[2] The authors take this opportunity to thank Dr. J. G. Lipman and Prof. A. W. Blair for their kind permission to use soils from these plots and also certain unpublished data on crop yields from these soils for 1923.

amount of carbon dioxide formed, which we would naturally expect, since these soils are much richer in organic matter than the other soils, as indicated by their carbon and nitrogen content (table 6). The limed soils (5B) produced somewhat more carbon dioxide than the corresponding unlimed soil, which would tend to confirm the various observations that lime stimulates the decomposition of organic matter in the soil. Nearly one hundred milligrams of carbon dioxide were given off by the unlimed and more than one

TABLE 1

Respiratory power of soils

PLOT NUMBER	CO_2 PRODUCED FROM 1 KGM. SOIL IN 14 DAYS, BEGINNING AT VARIOUS DATES					AVERAGES
	4-11-22	7-10-22	8-18-22	4-3-23	6-26-23	
	mgm.	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*
5A	1327.07		855.81	1159.96	653.23	999.02
6A		1100.75	1160.37			1130.56
7A	155.60	290.16	254.01	244.04	260.02	240.77
9A			499.05	459.41		479.23
11A	551.98	356.15	358.65	354.48	470.26	418.30
19A			423.27			423.27
5B	1425.28				774.85	1100.07
7B	443.96	337.38		517.95	655.16	488.61
11B	666.37	387.60		459.42	578.94	523.08

TABLE 2

Respiratory power of soils

PLOT NUMBER	CO_2 PRODUCED FROM 1 KGM. SOIL IN 48 HOURS, BEGINNING AT VARIOUS DATES					AVERAGES
	4-11-22	7-10-22	8-18-22	4-3-23	6-26-27	
	mgm.	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*
5A	237.24		175.17	206.52	169.91	197.21
6A		182.86	210.82			196.84
7A	21.29	46.93	51.43	36.96	62.33	43.79
9A			122.14	88.27		105.21
11A	74.11	71.25	71.77	58.69	113.23	77.81
19A			90.32			90.32
5B	279.84				215.03	247.44
7B	80.63	66.24		95.65	201.56	111.02
11B	113.42	69.39		79.42	193.30	113.88

hundred milligrams by the limed soil in twenty-four hours. This is more than Stoklasa obtained (68–76 mgm.) for his most fertile sugar beet soils.

The lowest amount of carbon dioxide was produced by the unmanured, unfertilized and unlimed soil 7A, both in two days and in fourteen days. About 22 mgm. of carbon dioxide was given off the first day, which makes it somewhat more than what Stoklasa found in the case of very poor soils. The crop yields reported in table 6 will substantiate the fact that this is the

poorest soil while 5A, 6A and 5B are the most fertile soils in the series. It is important to note the very interesting correlation not only between the respiratory power of these soils with crop productivity but also with numbers of bacteria and nitrifying capacity, as reported in detail elsewhere (34, 36) and as shown in table 6.

Plot 11A has received yearly application of minerals and ammonium sulfate and that has become so acid that it does not support good crop growth; this plot showed a somewhat greater respiratory power than plot 7A. Here again, both two- and fourteen-day periods give comparable results and there is a definite correlation between the respiratory power and crop productivity. The plot receiving minerals only (19A), without any nitrogenous fertilizer or lime comes next to the ammonium sulfate plot in the respiratory power, but is higher in crop yield. This is possibly due to the fact that 11A supports a very abundant fungous flora, while conditions are not favorable for the growth of higher plants. The respiration of the fungi as well as the abundant growth of *acetosella* on 11A probably accounts for the somewhat greater evolution of carbon dioxide than would correspond to its crop production.

The plot receiving sodium nitrate and minerals (9A), the plot receiving lime only (7B) and the one receiving ammonium sulfate, minerals and lime (11B) follow in increasing order of their respiratory capacity. These plots merely show a general parallelism between the respiratory power, crop growth and other biological activities, but not as perfect as in the case of 5A or 7A. This is due to the interfering influence of liming. The addition of lime to an acid soil makes conditions more favorable for the activities of microorganisms, thus resulting in an increase in the numbers of bacteria (decrease of fungi) and an increase in the respiratory power of the soil. This is also accompanied by a greater liberation of plant food and increased crop yield. However, the two may not necessarily correspond, i.e. conditions may be made more favorable for the growth of microörganisms than for the growth of plants. This accounted, in the nitrification studies, for the greater stimulus of lime application to nitrification than to the growth of timothy. The respiratory power is increased somewhat less than the nitrifying capacity so that the results on the respiratory power both in unlimed and limed soils show a closer parallelism with crop yields.

The results on the decomposing power of the soil, when alfalfa is used as a source of organic matter are given in table 3. Here also, decided differences in the capacity of the soils to produce carbon dioxide correspond to their fertility; however, there is no pronounced parallelism. Alfalfa is decomposed in the soil by various groups of microörganisms, especially by fungi. The two poorest soils, 7A and 11A, are distinctly acid in reaction and have, probably as a result of that, an abundant fungous flora, especially 11A. When alfalfa is added to the soil, the fungi rapidly attack the fresh organic matter and a great deal of carbon dioxide is evolved. This will in part compensate for the otherwise lower microbiological activities of these plots in

comparison with the more fertile plots, especially those receiving manure or lime. For this reason, the power of the soil to decompose alfalfa is not considered a valuable index to the respiratory power, and the results are, therefore, not included in the summary shown by table (6).

Decomposition of dextrose as measured by the evolution of carbon dioxide gave results comparable with those obtained in the study of the respiratory power of the soil. However, the length of the incubation period should be short.

TABLE 3

Decomposing power of soils

PLOT NUMBER	CO_2 PRODUCED IN 7 DAYS, BEGINNING AT VARIOUS DATES					AVERAGES
	4-26-22*	7-24-22*	9-1-22*	4-17-23†	7-11-23†	
	mgm.	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*
5A	706.22		601.72	924.32	782.02	753.57
6A		596.84	613.69			605.27
7A	419.14	431.21	455.27	628.11	586.03	503.95
9A			589.82	684.91		637.37
11A	477.59	453.28	467.47	579.70	622.42	520.09
19A			559.04			559.04
5B	621.51				874.46	747.99
6B		603.84				603.84
7B	490.42	539.62		714.77	807.06	637.97
11B	474.13	546.69		699.43	802.10	630.59

* 1 gm. alfalfa meal added to 200 gm. soil.

† 1 gm. alfalfa meal added to 1 kgm. soil.

TABLE 4

Course of evolution of CO_2 from dextrose

PLOT NUMBER	PRODUCTION OF CO_2 IN 200 GM. SOIL TREATED WITH 0.5 GM. DEXTROSE, AFTER VARYING PERIODS OF INCUBATION			
	24 hours	48 hours	72 hours	96 hours
	mgm.	*mgm.*	*mgm.*	*mgm.*
5A	239.03	328.45	376.78	407.17
7A	53.83	147.88	260.45	327.01
7B	139.48	287.93	362.30	389.79

The carbon dioxide produced from 500 mgm. of dextrose added to 200-gm. portions of three soils of distinctly different fertility (5A, 7A and 7B) may serve as an index for differentiating these soils after 24, and even 48 hours of incubation (table 4). On prolonging the period of incubation, the differences gradually disappear. This is again due to the fact that all soils harbor organisms capable of decomposing dextrose, which organisms develop abundantly in all soils with prolonged incubation. This method depends upon the fact that the soil supporting the most abundant microbiological flora before treatment will effect the most rapid decomposition of the dextrose, particularly

during the first two days after its addition. Table 4 indicates the desirability of using a short period of incubation (24–36 hours) when dextrose is used. For this experiment the soils were sampled in the spring. In midsummer and in the fall, the same method indicated diminished production of carbon dioxide from dextrose per unit time, as shown in table 5. Whether this is due to changes in the physical and chemical conditions of the soils or merely their normal variability is not clear. The production of carbon dioxide for forty-eight hours seemed to bring out the greatest differences between the soils.

The amounts of carbon dioxide evolved from the soils from dextrose (decomposing power) are somewhat parallel to the carbon dioxide produced from the soils themselves (respiratory power), as well as to the crop productions

TABLE 5

CO_2 production from soils treated with dextrose

PLOT NUMBER	AMOUNT PRODUCED IN 48 HOURS FROM 100 GM. SOIL TREATED WITH 500 MGM. DEXTROSE			AVERAGES
	7-18-23	9-12-23	10-17-23	
	mgm.	*mgm.*	*mgm.*	*mgm.*
5A	248.76	162.39	175.65	195.60
7A	64.81	31.63	45.15	47.20
9A		91.99	78.60	85.30
11A	190.96		130.73	160.85
5B	304.19	215.20	159.67	226.35
7B	167.58	98.32	112.26	126.05
11B	184.37	96.94	113.30	131.54

and other biological activities (table 6). The two manured soils were most active, the limed (5B) more so than the unlimed (5A). The unmanured and unlimed soil (7A) was least active, and the soils receiving artificial fertilizers and lime were intermediate. Soils 11A and 9A were tested only twice, and, in view of the fact that the actual amounts of carbon dioxide in the different periods of examination were different, a comparison of the averages of the results from 11A and 9A, on the one hand, with the general averages of the rest of the soils, on the other, might not be justified. For this reason, the carbon dioxide production of these two soils from dextrose are not included in figure 2. The relatively larger amount of available nitrogen in soil 11A brought about by the yearly addition of $(NH_4)_2SO_4$, which is neither used up by the plants nor readily nitrified, as well as the great abundance of fungi probably account for the relative active carbon dioxide production from dextrose in this soil.

Comparisons between crop yields, numbers of microörganisms, nitrifying capacities, respiratory capacities and decomposing capacities of the different soils are given in table 6, and they are graphically represented in figure 4.

The courses of carbon dioxide evolution from 1 kgm. of the soil itself, and in the presence of added organic matter in the form of alfalfa meal based on the average of several different determinations, are given in figure 3.

In plotting figure 4, comparative numbers are used and the data are calculated with the highest figure in each set of determinations being taken as 100. In interpreting these results, it should be kept in mind that a microbiological analysis of a soil would indicate its present crop producing power without further fertilization. It should also give information as to the need of the soil for certain specific fertilizers, organic matter or lime. Of the soils studied,

TABLE 6

Chemical and biological conditions of the soils and their crop productions

PLOT NUMBER	TREATMENT	REACTION OF SOIL	NITROGEN CONTENT	CARBON CONTENT	TOTAL CROP YIELD PER ACRE		NUMBERS OF MICROÖRGANISMS PER GRAM	NITRIFYING CAPACITY† (NO_3-N IN 100 GM. OF SOIL)	CO_2-PRODUCING CAPACITY	
					1908–1922	1923 (Corn)			Respiratory (from 1 kgm. of soil in 14 days)	Decomposing (from 200 gm. of soil + 0.5 gm. dextrose in 48 hours)
		pH	*per cent*	*per cent*	*lbs.*	*lbs.*	*thousands*	*mgm.*	*mgm.*	*mgm.*
5A	Minerals + manure	5.5	0.1463	1.73	69,300	6,108	13,040	8.86	999.02	195.60
7A	Untreated	4.9	0.0826	0.96	15,464	1,710	5,600	2.08	240.77	47.20
9A	Minerals + $NaNO_3$	5.8	0.0994	1.17	57,968	5,273	9,600	6.62	479.23	85.30
11A	Minerals + $(NH_4)_2SO_4$	4.4	0.1064	1.23	41,754	1,753	5,300	2.16	418.30	160.85
5B	Minerals + manure + lime	6.7	0.1428	1.74	59,754	6,478*	12,500	12.07	1100.07	226.35
7B	Lime only	6.5	0.0868	1.18	30,160	5,566	9,800	7.87	488.61	126.05
11B	Minerals + $(NH_4)_2SO_4$ + lime	6.1	0.0952	1.10	61,906	6,440*	10,600	8.75	523.08	131.54

* Actual yield of corn grain was less in 5B than in 5A and was about the same in 11B as in 5A.

† See Waksman (36).

5A and 5B are seen to be the most fertile and 7A the least fertile. The actual crop production of these is actually correlated with the results obtained from a microbiological analysis. Soil 5A produced a larger crop yield during the 15-year period than 5B, but the yield of corn in 1923 was higher in 5B than in 5A. The numbers of bacteria are higher in 5A than in 5B, while the respiratory and decomposing powers, especially the latter, are higher in 5B; the nitrifying capacity of 5B is even still higher than of 5A. The reaction of 5B which is probably more favorable for the activities of the nitrifying bacteria and nitrogen fixing bacteria, is probably responsible for these differences.

The data for 7A are quite parallel, except for the numbers of microörganisms which appear higher than the other data. Here again, nitrification, crop yield, respiratory and decomposing powers are correlated.

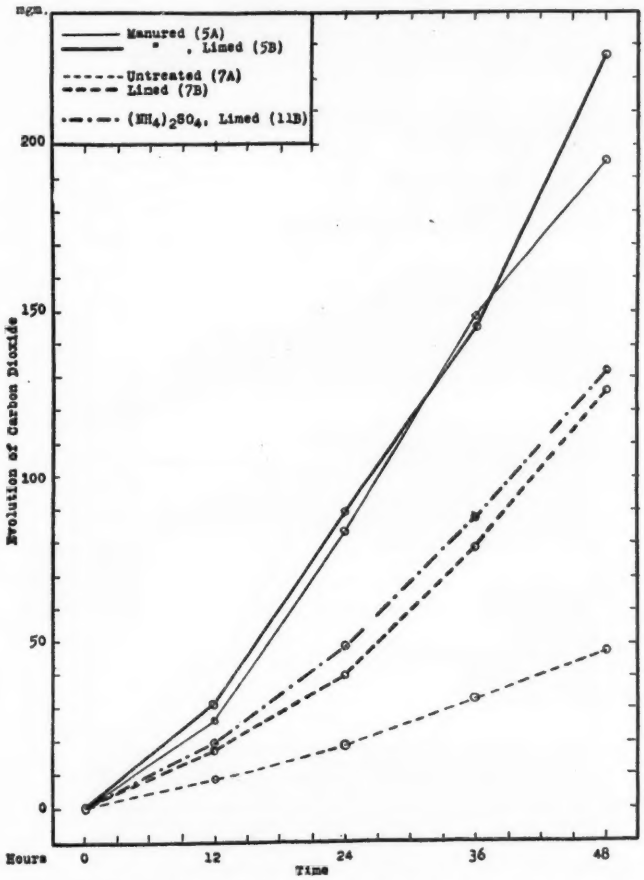


FIG. 2. COURSE OF CARBON DIOXIDE PRODUCTION FROM DEXTROSE ADDED TO SOILS OF DIFFERENT FERTILITY

The addition of lime to a soil which has been cultivated for 15 years, without any additional fertilizers (7B) greatly increased the crop yield. This may be due to the reaction (pH = 6.5) which favors the activity of the nitrogen-fixing bacteria, as will be shown in a subsequent contribution. The reaction also affects the other microbiological activities, the nitrifying and oxidative capacities and especially the number of microörganisms. The comparatively

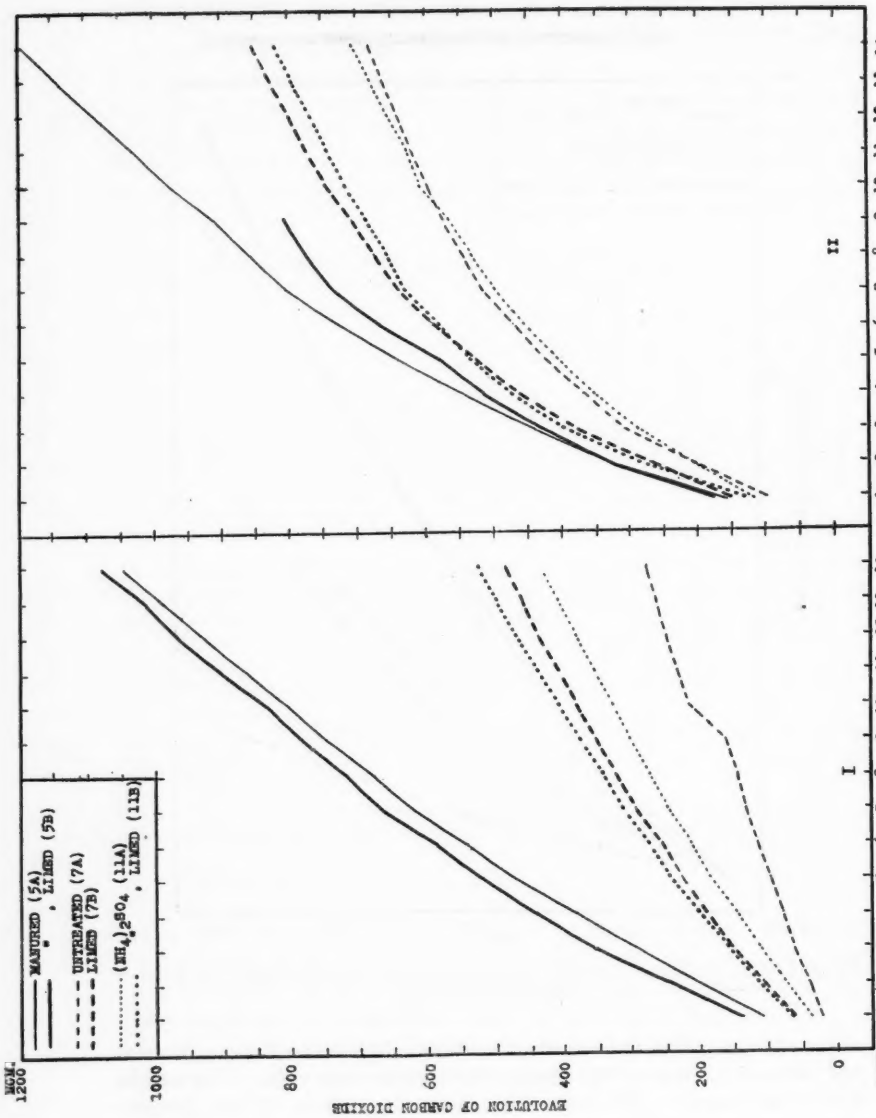


FIG. 3. EVOLUTION OF CARBON DIOXIDE FROM FRESH SOILS OF DIFFERENT FERTILITY WITHOUT FURTHER TREATMENT (I); AND IN PRESENCE OF 0.2 PER CENT ALFALFA MEAL (II)

TIME

FIG. 3. EVOLUTION OF CARBON DIOXIDE FROM FRESH SOILS OF DIFFERENT FERTILITY WITHOUT FURTHER TREATMENT (I); AND IN PRESENCE OF 0.2 PER CENT ALFALFA MEAL (II)

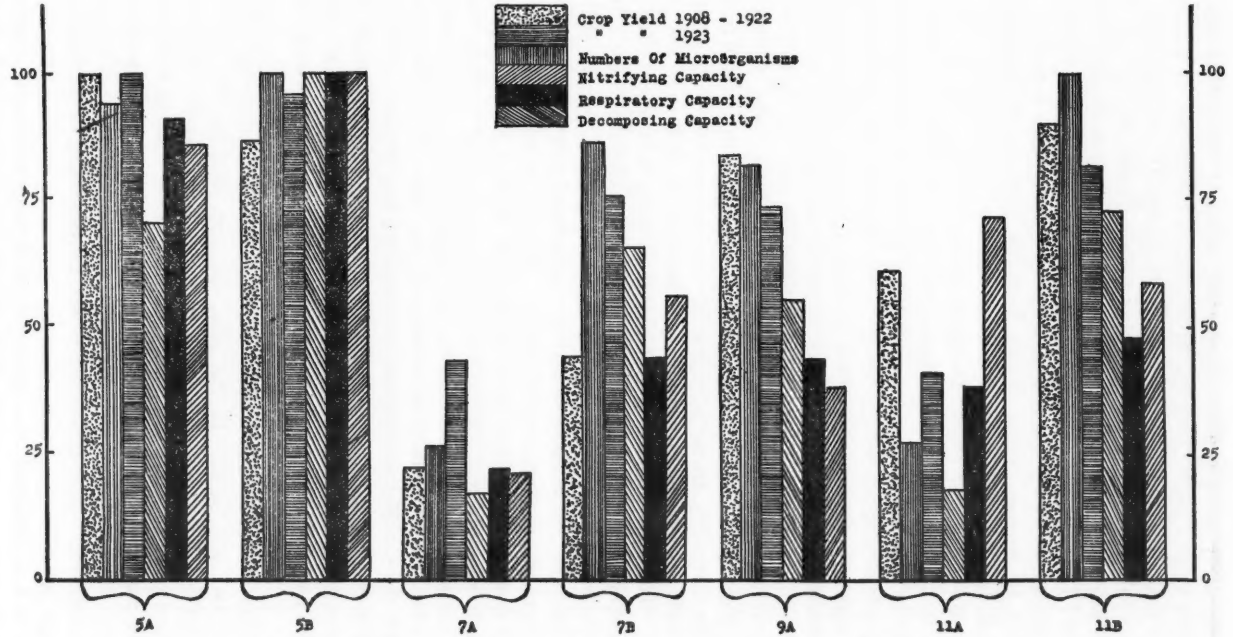


FIG. 4. CORRELATION BETWEEN MICROBIOLOGICAL ACTIVITIES AND CROP YIELDS

low respiratory power of this soil is caused rather by the low content of the available organic matter than by microbiological inactivity. It is interesting to note that although the carbon contents of 7A and 7B are almost the same, the respiratory power, or the amount of carbon dioxide produced by 1 kgm. of soil kept for fourteen days under optimum conditions, is nearly twice as high in 7B than in 7A. This serves also to emphasize the fact that it is not sufficient to determine the respiratory power of a soil as a measure of its capacity to produce carbon dioxide from the viewpoint of microbiological methods, but it is also necessary to determine the relative rapidity with which these solids decompose readily available sources of energy, like dextrose.

The fact that the mere use of inorganic fertilizers, without stable manure, green manure or lime will not work towards the formation of a soil supporting any active microbiological flora is brought out clearly in the results from soil 9A. Although the total crop yield has been kept very high, comparatively low numbers of microörganisms and especially the low nitrifying, respiratory and decomposing powers seem to indicate that the soil is not as active biologically in comparison with the crop yields as are the other soils. The fact that the respiratory and decomposing powers of a soil obtaining artificial fertilizers, as in the case of 9A, are not as high as its crop yield need not necessarily mean that these microbiological activities cannot serve as indices of soil productivity. These two factors—microbiological activity and soil productivity—need not of necessity be related. The one, crop production, is at any moment dependent to a large extent upon the inorganic nutrients present of the soil, while the other, microbiological activity, is regulated to a much larger extent by the abundance of soil organic matter. A soil composed of little else than quartz sand with available elements essential to plant growth may support plants temporarily and still lack any abundant microbial flora. In such cases the *microbiological activities* and *soil productivity* are not correlated but the first *may be better considered as forecasting the future possibilities of the soils.* So with these studies an abundant microbial life may better be considered to indicate that the soil has been built up to a state of fertility which is more permanent than when the microbial activity is considerably less. Although the two may not be correlated at any one time they both approach the same limit.

Similar results are obtained in the case of the soil receiving ammonium sulfate and lime (11B). In this case, the crop yield for 1923 was higher accompanied by a more abundant microbial flora, greater nitrifying and oxidative powers. Since the carbon content is about alike in both plots and the soil reaction is nearly alike, we would expect about the same respiratory powers. As a matter of fact, 11B, with a somewhat lower carbon content, has a somewhat higher respiratory power, corresponding to the better microbiological activities.

Soil 11A is abnormal; the continued use of ammonium sulfate resulted in a great increase in acidity (pH 3.9 to pH 4.4) and an abundant fungous flora.

The added nitrogen is not taken away by the plants and a part of it is probably present as absorption compounds of the zeolitic silicates and a part in the fungus mycelium. The crop yield has been constantly decreasing till in 1923 it is as low as in 7A, the soil receiving no fertilizer. The comparatively low numbers of bacteria, low nitrifying and respiratory powers go hand in hand with the low crop yield. However, the decomposing power of this soil is very high, probably due to the decomposition of the dextrose added, by the abundant fungus flora in the presence of the available nitrogen.

SUMMARY

Determination of the amounts of carbon dioxide evolved from the soils, both without and with the addition of small amounts of organic matter, can be used in grading these soils on the basis of their fertility as well as can determinations of the numbers of microörganisms and nitrification in the soils. The data presented in this paper together with those published previously on the microbiological analysis of soils allow us to look forward to the development of a group of quantitative methods for determining the productive capacity of the soil.

To measure the capacity of the soil to produce carbon dioxide, two methods are suggested: One, determining the amount of carbon dioxide formed from one kilogram of fresh soil, for fourteen days under optimum conditions of temperature and moisture; two, determining the amount of carbon dioxide produced from 500 mgm. of dextrose added to 100 gm. of fresh soil, in forty-eight hours.

Soils rich in organic matter produce by far the greatest amount of carbon dioxide (this does not apply to peats, mucks or such abnormal soils). The amount of carbon dioxide produced is not, however, proportional to the carbon content of the soils. The addition of lime to an acid soil stimulates the production of carbon dioxide, but not to as great an extent as nitrification. This is due to the difference in the nature of the organisms responsible for the chemical changes.

REFERENCES

(1) Darbishire, F. W., and Russell, E. J. 1907 Oxidation in soils and its relation to productiveness. Part II. The influence of partial sterilization. *In* Jour. Agr. Sci., v. 2, p. 305–326.

(2) Déhérain, P. P., and Démoussy, E. 1896 Sur l'oxydation de la matière organique du sol. *In* Ann. Agron., v. 22, p. 305–337.

(3) Dvořák, J. 1912 Studien über die Stickstoffanhäufung im Boden durch Mikroorganismen. *In* Ztschr. Landw. Vers. Sta. Oesterreich., v. 15, p. 1077–1121.

(4) Fraps, G. S. 1915 Oxidation of organic matter in soils. Texas Agr. Exp. Sta. Bul. 181, p. 5–27.

(5) Fred, E. B., and Hart, E. B. 1915 The comparative effect of phosphates and sulfates on soil bacteria. Wis. Agr. Exp. Sta. Res. Bul. 35, p. 35–66.

(6) Gainey, P. L. 1919 Parallel formation of carbon dioxide, ammonia and nitrate in soil. *In* Soil Sci., v. 7, p. 293–311.

(7) GEHRING, A. 1922 Beitrag zur Klärung der Düngewirkung organischer Substanzen. *In* Centrbl. Bakt. (etc.), v. 57, p.241–271.

(8) KISZLING, R., AND FLEISCHER, M. 1891 Die Bodenluft in besandeten und nicht besandeten Hochmoor- und Niederungsmoorböden. *In* Landw. Jahrb., v. 20, p. 876–889.

(9) KLEIN, M. A. 1915 Studies in the drying of soils. *In* Jour. Amer. Soc. Agr., v. 7, p. 49.

(10) KÖNIG, J., AND HASENBÄUMER, J. 1920 Die Bedeutung neuer Bodenforschungen für die Landwirtschaft. *In* Landw. Jahrb., v. 55, p. 185–252.

(11) KÖNIG, J., HASENBÄUMER, J., AND GLENK, K. 1923 Über die Anwendung der Dialyse und die Bestimmung der Oxydationskraft für die Beurteilung des Bodens. *In* Landw. Vers. Sta., v. 79–80, p. 491–534.

(12) LEATHER, J. W. 1915 Soil gases. *In* Mem. Dept. Agr. India. Pusa., Chem. Ser., v. 4, p. 85–134.

(13) LEMMERMANN, O., ASO, K., FISCHER, H., AND FRESENIUS, L. 1911 Untersuchungen über die Zersetzung der Kohlenstoffverbindungen verschiedener organischer Substanzen im Boden, speziell unter dem Einfluss von Kalk. *In* Landw. Jahrb., v. 41, p. 217–256.

(14) MERKLE, F. G. 1918 The decomposition of organic matter in soils. *In* Jour. Amer. Soc. Agron., v. 10, p. 281–302.

(15) NELLER, J. R. 1918 Studies on the correlation between the production of carbon dioxide and the accumulation of ammonia by soil organisms. *In* Soil Sci., v. 5, p. 225–239.

(16) NELLER, J. R. 1920 The oxidizing power of soil from limed and unlimed plots and its relation to other factors. *In* Soil Sci., v. 10, p. 29–39.

(17) PETERSEN, P. 1870 Ueber den Einfluss des Mergels auf die Bildung von Kohlensäure und Saltpetersäure im Ackerboden. *In* Landw. vers. Sta., v. 13, p. 155–175.

(18) PETTENKOFER, M. 1858 Ueber eine Methode die Kohlensäure in der atmosphärischen Luft zu bestimmen. *In* Chem. Soc. Trans., v. 10, p. 292.

(19) POTTER, R. S., AND SNYDER, R. S. 1916 Carbon dioxide production in soils and carbon and nitrogen changes in soils variously treated. Iowa Agr. Exp. Sta. Res. Bul. 39.

(20) RAHN, O. 1908 Bakteriologische Untersuchungen über das Trocknen des Bodens. *In* Centrbl. Bakt. (etc.), 2 Abt., v. 20, p. 38–61.

(21) RUSSELL, E. J. 1905 Oxidation in soils and its connection with fertility. *In* Jour. Agr. Sci., v. 1, p. 261–279.

(22) RUSSELL, E. J., AND APPLEYARD, A. 1915 The atmosphere of the soil: its composition and the causes of variation. *In* Jour. Agr. Sci., v. 7, p. 1–48.

(23) SEVERIN, S. A. 1910–1912 Die Mobilisierung der Phosphorsäuren des Bodens unter dem Einflusz der Lebenstätigkeit der Bakterien. *In* Centrbl. Bakt. (etc.), 2 Abt., v. 28, p. 561; v. 32, p. 498.

(24) STARKEY, R. L. 1924 Some observations on the decomposition of organic matter in soils. *In* Soil Sci. (to be published).

(25) STOKLASA, J. 1911 Biochemischer Kreislauf des Phosphat-Ions im Boden. *In* Centrbl. Bakt. (etc.), 2 Abt., v. 29, p. 385–519.

(26) STOKLASA, J. 1911 Methoden zur Bestimmung der Atmungsintensität der Bakterien im Boden. *In* Ztschr. Landw. Versuchs. Oesterreich, v. 14, p. 1243–1279.

(27) STOKLASA, J. 1912 Methoden zur biochemischen Untersuchung des Bodens. *In* Abderhalden's Handb. d. biochem. Arbeitsmeth., v. 5, pt. 2, p. 843–910.

(28) STOKLASA, J. 1922 Le rôle de l' acide carbonique dégagé par les microorganismes dans l'amélioration des terres cultural arables pour obtenir le meilleur rendement. *In* Compt. Rend. Agr. France, v. 8, p. 594–6.

(29) STOKLASA, J. 1922 Biochemical methods for the determination of the fertility of the soil. *In* Chemiker Zeitung, v. 46, p. 681–683; *ref. in* Chem. Abs., v. 17, p. 172.

(30) STOKLASA, J., AND ERNEST, A. 1905 Über den Ursprung, die Menge und die Bedeutung des Kohlendioxyds im Boden. *In* Centrbl. Bakt., 2 Abt., v. 14, p. 723–736; *also in* Ztschr. Zuckerind. Böhmen., v. 31, p. 291–401.

(31) TRUOG, E. 1915 Methods for the determination of carbon dioxide and a new form of absorption tower adapted to the titrimetric method. *In* Jour. Indus. Engin. Chem., v. 7, p. 1045–1049.

(32) VAN SUCHTELEN, F. H. H. 1910 Über die Messung der Lebenstätigkeit der aerobiotischen Bakertien im Boden durch die Kohlensäureproduktion. *In* Centrbl. Bakt. (etc.), 2 Abt., v. 28, p. 45–89.

(33) VAN SUCHTELEN, F. H. H. 1923 Energetik und die Mikrobiologie des Boden. *In* Centrbl. Bakt. (etc)., 2 Abt., v. 58, p. 413–430.

(34) WAKSMAN, S. A. 1922 Microbiological analysis of soil as an index of soil fertility. III. Influence of fertilization upon numbers of microörganisms in the soil. *In* Soil Sci., v. 14, p. 321–346.

(35) WAKSMAN, S. A. 1922 Microbiological analysis of soil as an index of soil fertility. IV. Ammonia accumulation (Ammonification). *In* Soil Sci., v. 15, p. 49–65.

(36) WAKSMAN, S. A. 1923 Microbiological analysis of soil as an index of soil fertility. VI. Nitrification. *In* Soil Sci., v. 16, p. 55–68.

(37) WAKSMAN, S. A., AND STARKEY, R. S. 1923 Partial sterilization of soil, microbiological activities and soil fertility. *In* Soil Sci., v. 16, p. 137–158, 247–268.

(38) WOLLNY, E. 1880 Untersuchungen über den Kohlensäuregehalt der Bodenluft. *In* Landw. Vers. Sta., v. 25, p. 373.

(39) WOLLNY, E. 1897 Die Zersetzung der organischen Stoffe und die Humusbildungen mit Rücksicht auf die Bodenkultur. C. Winter, Heidelberg.

THE QUANTITATIVE DETERMINATION OF NITRATES IN SOIL

D. J. R. VAN WIJK

Department of Agriculture, Union of South Africa

Received for publication July 12, 1923

METHODS IN USE

Many methods have been devised for carrying out this important determination; some give very reliable results under particular circumstances only, while others are of doubtful merits and are quite inapplicable when very small quantities of nitrates are under consideration.

Of the more common methods Grandval and Lajoux's phenoldisulfonic acid method is perhaps the best known. One modification of the method is described in full by Fraps, (12, p. 10–12) and it appears to be used very extensively. But very serious objections have been raised against its use when applied to soils containing appreciable amounts of salts (4). Chlorides especially interfere very much (30). Organic matter also vitiates the results (27, 33) obtained by its use. In order to make the method more general, modifications have been introduced by various workers, among whom may be mentioned, Perrier and Farcy (25), Syme (33), Farcy (11), Caron and Raquet (7), Chamot, Pratt and Redfield (8), Gericke (14), Nichols (23), Frederick (13), and Noyes (24). The method is therefore unreliable unless by preliminary work on the soil we find out what particular precautions should be taken. Moreover, as it is sometimes necessary to add a flocculating agent when obtaining the soil solution, further complications are introduced. Other colorimetric methods suffer from the same drawbacks.

It is sometimes necessary to estimate very small quantities of nitrates. In such cases all gasometric methods of estimation are inapplicable, as the unavoidable experimental errors become relatively too large. The impracticability of carrying out a large number of determinations at the same time and the cost of apparatus further militate against their use.

Busch (5) has devised a gravimetric method for estimating nitrates. Nitrates form an insoluble compound with "nitron" (diphenyl-endanilo-dihydro-triazole) in the presence of acetic acid. The method gives very accurate results when pure nitrate solutions are employed. But it breaks down in the presence of certain acids, salts and other substances found in the soil, since it also forms insoluble compounds with these. The crystallization of the insoluble nitrate compound is also interfered with when much organic matter is present. Some of these difficulties are discussed by Litzendorff (20). Even under the most favorable circumstances as far as extraneous matter is concerned, it is unreliable when the amount of nitrate is very small, since the experimental error introduced by washing and weighing becomes too great. The cost of the nitron is often prohibitive when a large number of determinations have to be done. The method as applied to pure nitrate solutions and also in the case of some mixtures has been rigorously investigated by Collins (9).

In a large number of methods the underlying principle is the reduction of the nitrates to ammonia, and the subsequent estimation of the ammonia. The best known of the methods belonging to this group are the zinc-copper couple method, the Ulsch acid reduction method, the Devarda alkaline reduction method, and the aluminum alkaline reduction method.

Objections have been raised against all these methods, and modifications have been introduced in some cases in order to overcome the difficulties encountered.

Purvis and Courtauld (28) have shown that the presence of albuminous matter interferes with the accuracy of the zinc-copper couple method. The nitrates are sometimes not completely reduced, while in other cases ammonia is formed from the organic matter present. The time and labor required in the preparation of the couples makes the method unsuitable when a large number of determinations are to be carried out simultaneously.

The Ulsch (34) acid reduction method is strongly recommended by Greaves and Hirst (15). Burgess (4) finds difficulties of technique in it, which, in the case of numerous determinations, would render the method impracticable. A critical examination of the method will be found further on in this paper.

In the Devarda method (10) an alloy of aluminum, copper and zinc is used, and the reduction is carried out in alkaline solution. Here again modifications had to be introduced. Allen (1) claims that the accuracy of the method as modified by him is limited only by the unavoidable error attaching to the measurement of the standard solutions. Russell (29) describes further improvements. Whiting, Richmond and Schoonover (37) substitute sodium peroxide for the hydroxide. Many of these improvements make the determination too involved or require special apparatus and are, therefore, unsuitable when several nitrate determinations are to be carried out together. Cahen (6) has shown that very reliable results are to be obtained when pure nitrate solutions are under consideration. Mitscherlich (22) finds the reduction complete when carried out in strongly alkaline solution. According to Greaves and Hirst (15) organic matter interferes in the method.

We have not been able to find any information about the applicability of the Devarda method to determinations of very small amounts of nitrates. The titration of the ammonia produced seems to be the general practice. In soils containing only about two parts per million of nitric nitrogen very large amounts of the soil have to be extracted, which will in general be extremely inconvenient, or else the unavoidable error of titration will make the determination worthless. To take an example, let the extract equivalent to 250 gm. of soil containing 2 parts per million of nitric nitrogen be reduced and the ammonia evolved collected in standard 0.1 *N* acid. One cubic centimeter of this acid is equivalent to 1.4 mgm. of nitrogen and the total nitrogen under consideration is only 0.5 mgm. We shall therefore have a titration of less than 0.4 cc. The relative magnitude of the experimental error is obvious.

The aluminum reduction method described by Burgess (4) is simple to carry out, and requires no special apparatus or reagents. He has shown it to be very reliable under a number of varying conditions which are likely to occur when working with soil solutions. He has applied it to solutions in which the amount of nitric nitrogen is relatively large and titration with 0.1 *N* acid could be resorted to. The reduction was practically complete. The author of this paper has successfully applied the method, with certain modifications, to the estimation of very small quantities of nitrates, where it was necessary to Nesslerize the ammonia produced. A large number of duplicate determinations were done by the modified method, as described in full further on in this paper, and very satisfactory results were obtained.

A discussion of the above methods and other methods in use, together with a long list of references, is given by Greaves and Hirst (15) in their paper entitled "Some factors influencing the quantitative determination of nitric nitrogen in the soil."

METHODS OF EXTRACTION

In every investigation on the amount of nitric nitrogen in a soil it is necessary in the first place to obtain a solution of this nitrate, so that it may be separated from the bulk of the soil. Many methods of obtaining this soil extract are in use, but none are ideal and some are quite useless when the nitrate is subsequently determined colorimetrically.

Organic matter interferes in most of the methods, and it is therefore desirable to have the soil extract free from it. The Pasteur-Chamberland filter gives a clear solution (31). But

it occasions slight losses of nitrates (2, p. 31). The time factor when working with heavy soils will be very variable and where a long time is taken for filtration changes in the nitrate content are likely to occur on account of bacterial activity, even if the filter is thoroughly cleaned and sterilized before each filtration.

The centrifuge was tried on soils rich in soluble salts and having a high clay or organic colloid content by Hirst and Greaves (16). They found that some solutions were not clear after 30 minutes centrifuging.

Suitable flocculating agents have therefore been resorted to. There exists a great divergence of opinion about the efficacy of some of these substances. Among the more common flocculating agents there are aluminum sulfate, aluminum chloride, ferric sulfate, sodium chloride, hydrochloric acid, potassium alum, iron alum, sodium alum, calcium carbonate and lime. Sulfates, chlorides, hydrochloric acid and aluminum and iron salts may not be used when the nitrate is subsequently determined colorimetrically. Where lime is used together with chloroform as an antiseptic, the colorimetric method also fails.

Greaves and Hirst (16) consider potassium alum the most suitable flocculating agent. The flocculating power of twenty-two common acids and salts on a highly puddled Hawaiian clay soil was investigated by McGeorge (21). He found aluminum sulfate to be the most active substance. The divalent calcium and magnesium salts of nitric, hydrochloric and sulfuric acids are next, while the monovalent salts of sodium, potassium and ammonium are least active. The acids are stronger than any of their divalent salts but the trivalent salt, aluminum sulfate, is stronger than any of the acids.

Potter and Snyder (26) use calcium carbonate as flocculating agent and prefer it to calcium oxide. Burgess (4) uses lime and gets practically complete recovery of nitrates. Wolkoff (39) found aluminum compounds the most suitable for flocculating clay. Lipman and Sharp (19) recommend the use of quicklime, and state that the use of 2 gm. of CaO to 100 gm. of soil gave the whole of the nitrate nitrogen in a soil of known nitrate content.

Noyes (24) recommends the use of calcium hydroxide as being the best precipitant of colored organic matter. Dilute hydrochloric acid (approximately 0.5 per cent) is used as a settling agent by Whiting, Richmond and Schoonover (37). Whiting and Schoonover (38) state "a large number of substances such as water, alkalies, alkaline earths and other carbonates, oxides, neutral salts, and various acids have been tried for securing an extract, but the results have shown hydrochloric acid to be the best deflocculating and settling agent as well as a superior agent in assisting in freeing the nitrate."

The other factors to be taken into consideration in obtaining the soil extract are the amount and condition of the soil, the ratio of soil to water, and the time of extraction. Here also we find a great divergence in the methods adopted by different workers.

Burgess (4) takes 100 gm. of the soil in an enamelled cereal dish, 2 gm. of powdered CaO and 200 cc. of water are added. The contents are thoroughly ground and mixed with a pestle for 3–5 minutes, after which the soil and clay are allowed to settle for 15 to 20 minutes, and the solution then filtered through paper.

Whiting and Schoonover (38) take 70–80 gm. of the oven-dried sample which had been placed in a 400-cc. shaker bottle. They add 300 cc. of hydrochloric acid (approximately 0.2 per cent) and shake in a mechanical shaker for 3 hours. The mixture is allowed to settle overnight.

Stewart and Peterson (32), working on the nitric nitrogen of the country rock, place 100 gm. of the finely ground rock in a large bottle with 1000 cc. distilled water, and shake for 16 hours in a shaking machine. The solution is then separated through a Pasteur-Chamberland filter.

Kelly (17) takes 200 gm. of dry soil in a flask; 500 cc. of water are added, and the flask is then vigorously shaken once every ten minutes for an hour and then filtered through a Pasteur-Chamberland filter.

Noyes (24) takes 50 gm. of soil and shakes for a minute with 200 cc. water. The mixture is shaken again after half an hour, and again after another half hour. Five grams of CaO is sometimes added before the 200 cc. water, if there is a probability of the solution not being clear.

Wahnschaffe (35) adds 2000 cc. water to 1000 gm. of fine air-dried soil, and shakes for 48 hours.

Buhlert and Fickendey (3) have investigated the influence of the time of shaking and the amount of water on the nitrate determination, as well as the difference produced when the soil is air-dried, or oven-dried at 100°C. They suggest drying the soil at 60–70°C. since bacterial activity ceases at 55°C. They found that shaking three times during 10 minutes was not sufficient to give all the nitrate. But 20 minutes shaking gave the maximum. They also recommend the addition of 2 per cent sodium chloride to clarify the extract. Two kilograms of soil together with 2–3 liters of water should be shaken for a ¼ minute at intervals of 5 minutes, and the process continued for 30 minutes.

Russell (29) dries at 55°C. and takes 200–500 gm. of the dried soil, and presses it firmly in a Büchner funnel fitted to a filter flask. Water is poured over the surface of the soil and the filtrate collected. At least 300 cc. should be collected for the nitrate determination. He considers that nearly all the nitrates are washed out by the first 300 cc. of filtrate.

Greaves and Hirst (15) have concluded that nothing is to be gained by shaking 100 gm. of soil with 2 gm. of alum and 500 cc. water longer than 5 minutes in a mechanical shaker. They qualify their statement however by saying "It must be borne in mind that these tests

TABLE 1

Nitric nitrogen in soil

	WITHOUT PREVIOUS DRYING	AFTER DRYING AT 58–63°C.
	p.p.m.	*p.p.m.*
a	14.45	16.78
b	14.31	16.90
Average..... ...	14.38	16.84

were carried out on finely powdered soil and not upon lumps." We could not find out exactly what was meant by "finely powdered soil." They have also investigated the effect of different ratios of soil to water on the nitrate determination, and conclude that the ratio is immaterial, provided there is not sufficient nitric nitrogen present to give a saturated solution.

Whenever the process of extraction takes some time there is the danger of bacterial activity changing the amount of nitrate. The use of an antiseptic then becomes desirable. Chloroform is probably the most common one in use. Greaves and Hirst (15) have investigated this point, and they conclude that there is very little danger of a change in the nitrate content taking place during the first few hours after adding the water for extraction. If 2 gm. of alum have been used as flocculating agent they consider no other antiseptic necessary, unless the solutions are to remain several hours, when 0.5 cc. chloroform will be sufficient to inhibit all bacterial activity.

It only remains to be added that special precautions must be taken when soil samples are taken in which nitrates are to be determined. Russell (29) states that the samples must be dried without any delay at 55°C. Even then a change of the nitrate content can take place in some soils. We have taken a sample of moist soil, and by duplicate determinations have obtained the amount of nitrate present in a uniform portion of it with the least possible delay, without previous drying. The remaining portion was weighed and dried for 18 hours as soon as possible in an oven at a temperature of 58–63°C. It was weighed again, and from

the results the amount of moisture calculated. Nitrates were determined in this dry portion. On calculating the amount of nitrates in the wet portion to the dry basis the results given in table 1 were obtained.

We thus see that there is a gain of very nearly 2½ parts per million. These results were obtained with a very heavy soil. The wet sample was therefore of a very lumpy nature. It probably took a long time before 55°C. was reached inside the lumps and in the warm damp soil bacteria probably became very active for a while. This would account for the increase in nitrates.

The determination of nitrates in the average laboratory soil sample which has been left lying in storage without thorough drying is of very doubtful value.

According to Waynick (36) a very large number of samples must be taken even from an apparently uniform area of limited extent in order to give a truly representative sample on mixing. He considers 10 or 16 a very limited number of samples.

THE ALUMINUM REDUCTION METHOD COMPARED WITH THE ULSCH METHOD

Allen (1) contradicts Burgess and states that the aluminum reduction method breaks down utterly in the presence of much organic matter of the type yielded to water by soils. This might be the case if the reduction is carried out in the aqueous extract from which nothing has been precipitated by lime. But if carried out as done by Burgess on an extract from which most organic matter has been precipitated by lime and filtered, we disagree entirely with Allen. We have done a number of determinations where a known quantity of nitrate has been added to the soil solution, and in every case recovery was almost complete.

Greaves and Hirst (16) state that "Conclusive evidence has been produced to show that when lime is used in the determination of nitric nitrogen by the phenoldisulfonic acid, the aluminum reduction or the Ulsch reduction methods low results are obtained." They refer to Potter and Snyder (26) for the results obtained by the aluminum reduction and to their own figures (15) in the case where the Ulsch method is used. They also state "this is not due to the lime carrying out with the colloid some of the nitrate, for similar results are obtained when lime is added to a pure solution of sodium nitrate and the nitric nitrogen is determined directly by the Ulsch method." In another article (16) they state that lime interferes with the determination of nitric nitrogen and can be discarded.

We have added lime to a solution of pure KNO_3 of known nitrate content, filtered, after shaking up well, and then reduced the nitrate in the filtrate by the aluminum reduction method. The recovery was complete to all intents and purposes, as is shown by table 2.

From general chemical considerations it seems rather strange that lime water should interfere with the estimation when pure solutions are employed. It is to be remembered that Greaves and Hirst (16) recommend the use of alum for flocculation as causing the least loss of nitrates. The conclusive evidence against the use of lime and the superiority of alum carry very little weight when some of their published figures are examined. The following table can be drawn up using the figures given by them (15, p. 184–185). It

must be remembered that each figure given by them is an average of from two to four separate determinations. A heavy clay soil and a greenhouse loam soil with a high percentage of organic matter were used to compare the results obtained by the Ulsch reduction, aluminum reduction and phenol-disulfonic acid methods, using different methods of obtaining a clear solution.

TABLE 2

Nitric nitrogen recovered from solution of KNO_3 by the aluminum reduction method

	TREATMENT OF KNO_3	AMOUNT OF NITRIC NITROGEN ADDED	AMOUNT NITRIC NITROGEN RECOVERED	AVERAGE	AVERAGE RECOVERY
		mgm.	*mgm.*	*mgm.*	*per cent*
a	No CaO added	2.53 2.53	2.51 2.41	2.46	97.2
b	4 gm. CaO 0.5 cc. $CHCl_3$	2.53 2.53	2.69 2.59	2.64	104.2

TABLE 3

Effect of flocculating agents on recovery of nitric nitrogen from soil

METHOD	SOIL	NITRIC NITROGEN ADDED TO SOIL	NITRIC NITROGEN RECOVERED	
			CaO as flocculating agent	K-alum as flocculating agent
		mgm.	*mgm.*	*mgm.*
Aluminum reduction method	Heavy clay	....	0.32	0.46
		10	9.49	9.85
	Greenhouse loam	....	2.17	1.61
		10	11.83	11.91
	Totals		23.81	23.83
Ulsch method	Heavy clay	....	0.88	0.70
		10	10.51	10.37
	Greenhouse loam	....	2.52	2.28
		10	12.19	12.12
	Totals		26.10	25.47

From table 3 we see that where the aluminum reduction method is used CaO and potassium alum have practically the same effect if the totals are considered. But with the Ulsch method we find that without exception higher results are obtained where lime is used. If the totals under CaO and potassium alum are taken we find 49.91 mgm. nitric nitrogen recovered where CaO is used, and only 49.30 mgm. where the alum is used. From these figures we might feel inclined to say that potassium alum causes a bigger loss

of nitrate than lime, which is the very opposite of Greaves and Hirst's contention.

It appears however from the above figures that more nitrate is recovered by the Ulsch method than by the aluminum reduction method. A critical examination was therefore made of the tables given by Greaves and Hirst from which the above figures were obtained. They applied the two methods to solutions obtained by nine different ways of clarifying—filter, centrifuge, CaO, $CaCO_3$, talc, potassium alum, sodium alum, iron alum, and ferric sulfate. Table 4 can be constructed for the two soils on working out the averages of the figures given.

If the results obtained by the Ulsch method are taken as standard and those by the aluminum reduction method compared with them on a percentage basis, we find that the recovery of nitrate by the aluminum reduction method is directly proportional to the concentration of the nitrate. Only

TABLE 4

Average nitric nitrogen recovered from soil

SOIL	NITRIC NITROGEN ADDED TO SOIL	ULSCH METHOD		ALUMINUM REDUCTION METHOD		RECOVERY BY ALUMINUM REDUCTION METHOD TAKING ULSCH METHOD AS STANDARD
		Amount recovered	Number of determinations	Amount recovered	Number of determinations	
	mgm.	*mgm.*		*mgm.*		*per cent*
Clay	.....	0.65	30	0.36	28	55.8
	+10	10.41	30	9.58	28	92.0
Greenhouse loam	.....	2.48	28	1.93	27	77.7
	+10	12.31	28	11.43	27	93.1

55.8 per cent is recoverable where 0.65 mgm. of nitrogen is reduced while 93.1 per cent is obtained when 12.31 mgm. of nitrogen is reduced. That the reduction should become more and more complete the larger the amount of nitrate to be reduced is against our experience. And from the nature of the chemical reaction it certainly seems extraordinary. We have done a large amount of work which involved the reduction of very small amounts of nitric nitrogen (.25–2.5 mgm.) by the aluminum reduction method, and have found the reduction of such small quantities complete to all intents and purposes, in fact there was a tendency to get rather more than 100 per cent. Such reductions have also been carried out with soil solutions to which a small known amount of nitrate had been added, with the same result. We incline, therefore, to the view that a constant plus error is involved in the determinations of Greaves and Hirst by the Ulsch method. That method which gives the greatest amount of nitrate is not of necessity the most reliable method.

We have tried using alum as a flocculating agent, but found that as much nitrogen was recovered from the blanks as from the solutions from soil treated with nitrates.

In the above discussion we have not considered the corresponding figures obtained by the phenoldisulfonic acid method, where such were given. If any nitrites are present they will behave like nitrates when the reduction methods are employed and will also be reduced to ammonia. But in the direct colorimetric method the nitrites yield a yellow coloration the intensity of which is equivalent to that given by a quantity of nitrate containing one-third of the amount of nitrogen present in the nitrite (27). Kelley (18, p. 432) gives figures showing the wide range of results obtained by the use of different methods when applied to soils containing a high concentration of nitrogenous material. Table 5 is quoted from his paper.

TABLE 5

Effects of nitrite on the determination of nitrate

	NITRITE NITROGEN	NITRATE NITROGEN BY MODIFIED COLORIMETRIC METHOD	NITRATE NITROGEN BY THE USUAL COLORIMETRIC METHOD	NITRATE NITROGEN BY ALUMINUM REDUCTION METHOD
	p.p.m.	*p.p.m.*	*p.p.m.*	*p.p.m.*
Soil plus 1 per cent of dried blood incubated for 46 days.....	275	22	30	283

TABLE 6

Nitric nitrogen obtained from three soils on using different amounts of lime

AMOUNT OF CaO USED	NITRIC NITROGEN RECOVERED		
	Soil A	Soil B	Soil C
gm.	*p.p.m.*	*p.p.m.*	*p.p.m.*
2	2.14 2.16		
4	2.48 2.67	2.48	1.50
5		2.51	1.56

Since we adopted lime as a flocculating agent we considered it necessary to investigate the effect of the quantity of lime used on the amount of nitrate found by the aluminum reduction method. Greaves and Hirst (16) state that when lime is used as a flocculant the quantity of nitric nitrogen recovered is inversely proportional to the quantity of lime added to a soil-water mixture. From the results of our trials we cannot substantiate their statement. Table 6 shows the results of our experiments on this point.

From our results it appears that there is certainly not less nitrate when more lime is used, in fact there is a slight gain. The phenomenon underlying this slight gain is at present being investigated.

MODIFICATIONS INTRODUCED INTO THE ALUMINUM REDUCTION METHOD

An ideal method for estimating nitrate would be one which conforms to the following requirements:

(1) It must be applicable to all cases, so that no preliminary work is necessary on the soil in order to find out whether it can be adopted.
(2) It must give accurate results.
(3) The ordinary equipment of the average laboratory should suffice for the determination, and it should be independent of chemicals difficult to procure.
(4) It must not involve undue time and labor.

Such a method, which gives good results where fairly large quantities of nitrates are involved, is described by Burgess (4). It is very simple to execute, and he has shown it to be applicable in cases where the phenol-disulfonic acid method fails hopelessly. The method, in principle, was adopted by the author in work which involved the determination of small quantities of nitrates in a large number of soil samples.

It had to be modified, however, in order to obtain greater accuracy. The soils on which most of the work was done rarely contained more than 3 parts per million of nitric nitrogen. The titration of ammonia with 0.1 *N* HCl after reduction, as carried out by Burgess, is therefore not accurate enough. In 50 gm. of a soil containing 3 parts per million of nitric nitrogen there will be after reduction an amount of ammonia equivalent only to about 0.1 cc. 0.1 *N* HCl. The titration error alone therefore will represent anything from 25–50 per cent of the total amount. And even with the concentrations used by Burgess we find that the figures given by him in the second decimal place are quite worthless, in view of the titration error involved.

It was impracticable to use very much more than 100 gm. of soil for a determination, and it was also impossible in some cases to obtain more than 100 cc. filtrate, out of the 200 cc. water added, in which to determine the nitrates.

We were thus compelled to adopt a colorimetric method for estimating the ammonia produced on reduction. Very consistent results were then obtained, as will be shown further on in this paper.

Since it was sometimes impossible to obtain 100 cc. filtrate when only 2 gm. of CaO was added, as done by Burgess, we used 4 gm. instead. After stirring with 200 cc. water, and filtering, it was then always possible to get at least 100 cc. filtrate.

The process of stirring the soil with water was also abandoned since from some of our results it appeared doubtful whether all the nitrates came into solution in the tedious operation of stirring by hand. Mechanical shaking was resorted to for the following reasons:

(1) There was no chance of any lumps of soil remaining unbroken.
(2) Conditions could be made exactly similar in different determinations, and did not involve the personal factor of stirring.

(3) Duplicate determinations agreed better after shaking than after stirring.

(4) It involved practically no extra work. The time factor was greater, but 0.5 cc. chloroform was added before commencing to shake, in order to eliminate all possibilities of bacterial activity.

On account of the very small amount of nitrate we were working on, we did not investigate the minimum time required for shaking, in order to bring all the nitrates into solution. We therefore adopted an arbitrary period. The sample of soil was shaken with 200 cc. water in the bottle for 90 minutes. This brought about what appeared to be complete disintegration of the aggregates of soil particles; 4 gm. of CaO were then added and the shaking continued for another 30 minutes. After this the mixture was filtered through a ribbed filter paper.

TABLE 7

Effects of area and distribution of aluminum sheets

NATURE OF STRIPS	AMOUNT OF NITROGEN ADDED IN FORM OF KNO_3	NITROGEN RECOVERED	PERCENTAGE RECOVERY	
	mgm.	*mgm.*	*per cent*	
Small pieces	2.5	2.46	98.4	
Small pieces	5.0	4.84	96.8	
Four thin strips	2.5	2.38	95.2	
Four thin strips	5.0	4.72	94.4	
Three curls*	2.5	2.52	100.8	101.2
	2.5	2.54	101.6	
Three curls*	7.5	7.26	96.8	97.9
	7.5	7.41	98.8	

* Total weight of three curls = 1.2 gm.

The aluminum used in the work consisted of strips cut from thin aluminum sheet. The influence of the area of the strips used and their distribution in the liquid containing the nitrate was investigated with the results shown in table 7. Instead of test tubes, 300 cc. wide-mouthed Erlenmeyer flasks were used since they were easier to manipulate. The strength of the NaOH used was 1 per cent and it occupied a volume of 150 cc. The aluminum was placed in the flasks in the following forms:

(1) One large strip, 1 cm. wide and 9 cm. long cut up into small pieces.

(2) Four thin strips, each 0.25 cm. wide and 18 cm. long.

(3) Three strips, each $\frac{1}{8}$ cm. wide, 15 cm. long, and curled into the form of a rough spiral which just goes through the neck of the flask, and has its parts more or less uniformly distributed throughout the volume of the liquid to be reduced.

The reductions were all done at room temperature. They were started late in the afternoon, and the ammonia formed was distilled off the next morning. The time of reduction was 17–19 hours and the room temperature, 21°–25°C. in summer. On some mornings in winter it was found to be as

low as 14°C. but this did not affect the results, as table 8 shows. This gives a recovery of 99.6 per cent. No use, therefore, was made of an incubator in the determinations.

If the reduction was done in an open flask there was a slight smell of ammonia to be noticed the next morning at the mouth of the flask; it was enough to turn red litmus blue when the moist paper was held over the solution. As the solution was not very alkaline it appeared that some of the ammonia was carried out of the liquid mechanically by the hydrogen evolved. It did not seem that the capillary tube used by Burgess to close off the open end of the test tube would prevent the escape of the ammonia as it was carried forward

TABLE 8

Recovery of nitrogen at a low temperature

TEMPERATURE IN MORNING	NITROGEN AS NITRATE IN SOIL ALONE		NITROGEN AS NITRATE ADDED TO SOIL	NITROGEN AS NITRATE RECOVERED		RECOVERY OF ADDED NITROGEN
°C.	*p.p.m.*		*p.p.m.*	*p.p.m.*		*p.p.m.*
14	2.63 2.52	2.58	25 25	27.22 27.74	27.48	24.90

TABLE 9

	AMOUNT OF NITRATE NITROGEN REDUCED	AMOUNT OF NITRATE NITROGEN PRESENT IN TRAP	MINIMUM LOSS IN TRAP	RECOVERY		AVERAGE PERCENTAGE RECOVERY
	mgm.	*mgm.*	*per cent*	*mgm.*	*per cent*	*per cent*
A	0.25	0.0115	4.6	.....	...	...
B	2.5	0.029	1.2	.....	...	...
C	0.25	.....	...	0.288	115	115
D	0.25	.....	...	0.288	115	
E	2.5	.....	...	2.40	96	99.6
F	2.5	.....	...	2.58	103.2	

by the hydrogen. We therefore substituted another form of trap. This consisted of a Soxhlet (sugar) tube with a narrow constriction, thrust through the hole of a rubber stopper fitted into the neck of the Erlenmeyer flask. The tube was packed with glass wool. When everything was ready for reduction and the stopper placed in position 0.1 *N* HCl (ammonia free) was poured over the glass wool. The constant evolution of hydrogen prevented the acid being sucked back beyond the constriction of the Soxhlet tube and any ammonia carried forward by the hydrogen was absorbed by the acid. This was all washed back into the flask before the solution was distilled.

Some investigation was done to determine the amount of ammonia which finds its way into the trap. Difficulty was experienced in removing the trap without allowing some of the acid to run back into the flask. But the results in any case show the minimum amount of ammonia collected by the trap.

Six separate determinations were done simultaneously, in four of which the liquid was washed back into the flask. Table 9 shows the results obtained.

Under these circumstances the determination can be considered quantitative. There is a tendency to get slightly high percentage when very small quantities of nitrate are reduced, but this is probably due to the concentration of the minute traces of ammonia in the water used for the determination.

After reduction the ammonia was distilled off into 10 cc. of 0.1 *N* HCl, and the distillate made up to a definite volume. Aliquots were then taken and Nesslerized. The experimental error introduced by comparing the tints produced with standard tints in Nessler tubes was found too large in view of the small quantities of nitrates the author was working on. Recourse was therefore had to the Schreiner Colorimeter. The only instrument available, after being slightly modified, was found to give very reliable results.

It was found inconvenient to move the eye laterally when viewing the colorimeter images and it also made accurate tint comparison unduly difficult. The mirror was therefore removed and cut in half vertically. The two halves were then placed at a slight angle so that both images could be viewed from the same point. This was found greatly to facilitate the comparison. When the work was first undertaken persistent increasing or decreasing ratios were obtained by the colorimeter, depending on the lengths of the columns. The following ratios taken at random, will serve as an example (1.03; 1.06; 1.06; 1.08; 1.13; 1.14; 1.18). This was found very annoying and the phenomenon was traced to the optical effect produced by the curvature of the inside bottom surfaces of both the outer and inner tubes of the colorimeter. The corresponding outer surfaces were optically plane. This irregularity in the glass was very much more pronounced in the small inner than the outer tubes; as was shown by the distortion produced in print when viewed through the tubes. It was remedied in the following manner: Water was poured into the inner tube. This minimized the lens effect at the bottom surface of contact, but the meniscus at the upper surface of the water now remained. A rubber ring was placed inside the top end of the tube, and sufficient water was poured in just to cover the upper edge of this ring. A microscope cover-glass was then placed so as to float by surface tension on the surface of the water, its upper surface remaining dry. Practically no distortion was now produced when print was viewed through the combination. In all subsequent work done with the modified colorimeter the ratios were found to be constant, and independent of the lengths of the columns of liquid.

In actual work with the colorimeter the following conditions were observed:

(1) The standard solution contained 0.03 mgm. of nitrogen in the form of ammonium chloride, and occupied a volume of 100 cc.

(2) All solutions to be compared had to be perfectly clear. A slight turbidity produced when the Nessler's solution contained any suspension interfered greatly with the accuracy.

(3) All solutions to be compared with the standard had to give ratios as close to 1 as possible.

(4) Solutions which had to be compared with each other had to be prepared at the same time.

(5) After mixing with Nessler's solution at least 20 minutes had to elapse before comparing tints since it was found that some ratios became constant only after that interval of time, especially if they deviated to any extent from 1.

After some practice with the method with all the improvements described above, it was possible to obtain very satisfactory results. The last set of eight determinations of nitrate gave the results shown in table 10. They represent four duplicate experiments.

The last column of figures is given in order to give an idea of the error involved if titration were resorted to instead of the Nesslerization. The average difference is equivalent to less than 0.02 cc. of 0.02 *N* acid.

TABLE 10

Nitrate nitrogen in dry soil

EXPERIMENT NUMBER	NITROGEN DETERMINED	AVERAGE OF DUPLICATES	DIFFERENCE BETWEEN DUPLICATES		DIFFERENCE IN NESSLERIZATION BETWEEN DUPLICATES	DIFFERENCE BETWEEN DUPLICATES CALCULATED TO 50 GM. SOIL
	p.p.m.	*p.p.m.*	*p.p.m.*	*per cent*	*mgm. of N*	*mgm.*
A	1.29 1.21	1.25	0.08	6.4	0.00165	0.0044
B	1.38 1.21	1.3	0.17	13.1	0.0021	0.0056
C	3.0 3.0	3.0	0	0	0	0
D	1.9 1.78	1.84	0.12	6.5	0.0024	0.006
Average	1.848	1.848	0.093	6.5	0.00154	0.004

TABLE 11

Summary of ninety-two nitrate determinations

	AVERAGE NITRIC NITROGEN	AVERAGE DIFFERENCE BETWEEN DUPLICATES		GREATEST DIFFERENCE BETWEEN DUPLICATES
	p.p.m.	*p.p.m.*	*per cent*	*p.p.m.*
First set: (0.94–4.51 p.p.m.)	1.892	0.111	5.87	0.27
Second set: (6.44–13.58 p.p.m.)	8.736	0.319	3.65	0.90

Taking the last 92 nitrate determinations done by the author consisting of 46 duplicate sets and omitting no results obtained, table 11 can be constructed. The reliability of the method can then be guaged from a consideration of the differences between duplicates. The results are arranged in two sets, the first set consisting of 62 individual determinations where the nitrate nitrogen ranges from 0.94 to 4.51 parts per million of oven-dried soil. The second set contains 30 separate determinations in which the range is from 6.44 to 13.58 parts per million.

No account was taken of "blanks" in the above work. A number of blank determinations were done, starting from different points in the process, as

well as for the complete process. In all cases the amount of nitrate found in a blank was extremely small, and seemed to vary more with different batches of ammonia-free water than with any other factor. It was also found that by far the greatest portion of this amount was produced during the last stage of the work, namely, the distillation of the reduced solution. A small amount of ammonia persistently adhered to the rubber connections of the distillation apparatus and could only be removed very slowly by the repeated boiling of ammonia-free water in the apparatus. This cannot, strictly speaking, be considered a "blank" since it is more of the nature of a "constant." Whatever ammonia is given off by the apparatus in any particular determination is replenished again from the ammonia distilling over. Care should however be taken, if great accuracy is desired, that soils with very divergent quantities of nitrate be not worked on at the same time (if aliquots representing the same amount of soil are taken for reduction) since the above "constant" may then vary. The true blank might then become appreciable. For the sake of completeness it may be stated that the blanks varied from 0.0040 to 0.013 mgm. of nitrogen per 100 cc. of distillate. Since less than 100 cc. of the distillate is generally taken for Nesslerization, we see that the effect of the blank may be considered negligible.

DESCRIPTION OF METHOD ADOPTED

The complete process for the determination of the nitrate in any soil may now be described in detail.

One-hundred grams of the oven-dried soil sample are placed in a shaking bottle, 200 cc. of distilled water, free from nitrates, is added, 0.5 cc. of chloroform is poured in, and the bottle closed. The bottle with its contents is shaken in a rotary shaker for 90 minutes. (This time factor has not yet been studied and much less time may suffice.) Four grams of CaO are introduced into the bottle and the shaking continued for another 30 minutes. The contents are then poured into a ribbed filter and filtration continued until a suitable amount of filtrate is obtained. This generally takes from ½ hour to 2½ hours with heavy soils. With some very clayey soils it is sometimes advantageous to filter from two funnels. An aliquot portion of the filtrate is then poured into a porcelain evaporating dish and 15 cc. of a 10-per cent solution of NaOH added. The mixture is boiled down to about one-third of the original volume in order to drive off any ammonia present. After cooling, the contents are washed over into a 300 cc. wide-mouthed Erlenmeyer flask with ammonia-free water. This flask has a mark made on its outside indicating the level of liquid when it holds 150 cc. It also contains three large curls of aluminum foil made from three strips each 15 cm. long by ½ cm. wide, the three together weighing about 1.5 gm. The curls should be arranged so as to occupy uniformly the space to be filled by the liquid. The flask is filled with water up to the 150 cc. mark after the nitrate solution has been transferred. A trap is then inserted into the mouth of the flask consisting of a rubber stopper

holding a Soxhlet (sugar) tube with a narrow constriction. The Soxhlet tube is packed with glass wool over which 0.1 *N* HCl is poured. This is generally done late in the afternoon, and the flask and its contents are left until the following morning, at room temperature. Reduction should then be complete. Where the night temperatures are very low (say below 15°C.) it would be advisable to use an incubator, and keep the temperature of reduction about 20°C. After 17–19 hours reduction the liquid in the trap is washed down into the reduction flask with ammonia-free water, and the liquid contents of the latter in turn washed into a 500 cc. distillation flask; 10 cc. of 10-per cent NaOH are added. The flask also contains a few pieces of granulated zinc in order to prevent bumping. After connecting to the condenser, the liquid, which should occupy about 250 cc. is brought to boiling and the distillate collected in 10 cc. 0.1 *N* HCl. The distillation is continued until the distillate and washings will almost fill a 200 cc. flask to the mark. After making up to the mark and shaking, suitable aliquots are taken for Nesslerization. The amount to be taken is found by trial, since it is necessary in an accurate determination that the colors given by the aliquot and the standard be very nearly the same. The Schreiner colorimeter with certain modifications is very suitable for comparing the tints. One cubic centimeter of the standard NH_4Cl solution containing 0.03 mgm. nitrogen is diluted to 100 cc. in the colorimeter tube. The aliquots are treated similarly. When all the solutions (if there is more than one nitrate determination) are made up to 100 cc. and mixed, 2 cc. of Nessler's solution are added to each. After shaking, at least 20 minutes should elapse before comparing the tints.

REFERENCES

(1) Allen, E R. 1915 Determination of nitric nitrogen in soils. *In* Jour. Indus. and Engin. Chem., v. 7, p. 521–529.

(2) Briggs, Lyman J., and Lapham, M. H. 1902 Capillary studies and filtration of clay from soil solutions. U. S. Dept. Agr. Bur. Soils, Bul. 19.

(3) Buhlert, H., and Fickendey, E.. 1906 Zur Bestimmung der Salpetersäure im Boden. *In* Landw. Vers. Sta., v. 63, p. 237–246.

(4) Burgess, P. S. The aluminum reduction method as applied to the determination of nitrates in "alkali" soils. *In* Univ. Cal. Pub. Agr. Sci., v. 1, no. 4, p. 51–62.

(5) Busch, M. 1905 Gravimetrische Bestimmung der Salpetersäure. *In* Ber. Deut. Chem Gesel., Jahrg. 38, v. 1, p. 861–866.

(6) Cahen, Edward 1910 A comparison of Pozzi-Escot's and Devarda's method for the estimation of nitrates. *In* The Analyst, v. 35, p. 307–308.

(7) Caron, H., and Raquet, D. 1910 Estimation of nitrates by the phenolsulphonic acid method. *In* Bul. Soc. Chim. Paris, ser. 4, v. 7, p. 1021–1025; *abs. in* The Analyst, v. 36, p. 84–85.

(8) Chamot, E. M., Pratt, D. S. and Redfield, H. W. 1911 Study of the phenolsulphonic acid method for the estimation of nitrates in water. III. Chief sources of error. *In* Jour. Amer. Chem. Soc., v. 33, p. 366–381; *abs. in* The Analyst, v. 36, p. 244.

(9) Collins, S. W. 1907 The "nitron" method for the estimation of nitric acid. *In* The Analyst, v. 32, p. 349–357.

(10) DEVARDA, A. 1892 Über die direkte Bestimmung des Stickstoffes im Salpeter. *In* Chem. Ztg., Jahrg. 16, p. 1952; *also in* Zeitschr. Analyt. Chem., v. 33, p. 113.

(11) FARCY, L. 1909 Estimation of nitrates by the method of Grandval and Lajoux in waters containing chlorides or nitrites. *In* Bul. Soc. Chim. Paris, ser. 4. v. 5, p. 1088–1092; *abs. in* The Analyst, v. 35, p. 81.

(12) FRAPS, G. S. 1920 Nitrification in Texas soils. Texas Agr. Exp. Sta. Bul. 259.

(13) FREDERICK, ROBERT C. 1919 An improved method for the estimation of nitrates in water by means of the phenolsulphonic acid reaction. *In* The Analyst, v. 44, p. 281–284.

(14) GERICKE, W. F. Nitrate estimations in the presence of chlorides. *In* Jour. Indus. and Engin. Chem., v. 9, p. 585–586.

(15) GREAVES, J. E., AND HIRST C. T. 1917 Some factors influencing the quantitative determination of nitric nitrogen in the soil. *In* Soil Sci., v. 4, p. 179–203.

(16) GREAVES, J. E., AND HIRST, C. T. 1922 The soil solution. *In* Jour. Indus. and Engin. Chem., v. 14, p. 224–226.

(17) KELLEY, W. P. 1918 Effect of nitrifying bacteria on the solubility of tricalcium phosphate. *In* Jour. Agr. Res., v. 12, no. 10, p. 671–683.

(18) KELLEY, W. P. 1916 Nitrification in semiarid soils: I. *In* Jour. Agr. Res., v. 7, no. 10, p. 417–437.

(19) LIPMAN, C. B., AND SHARP, L. T. 1912 Studies on the phenoldisulphonic acid method for determining nitrates in soils. *In* Univ. Cal. Pub. Agr. Sci, v. 1. no. 2, p. 21–37.

(20) LITZENDORFF, J. 1907 The use of nitron for the estimation of nitric acid in soils and plants. *In* Zeitschr. Angew. Chem., v. 20, p. 2209–2213; *abs. in* The Analyst, v. 33, p. 64–65.

(21) MCGEORGE, W. 1915 Effects of fertilizers on the physical properties of Hawaiian Soils. Hawaii Agr. Exp. Sta. Bul. 38.

(22) MITSCHERLICH, E. A. 1909 Eine quantitative Stickstoffanalyse für sehr geringe Mengen. *In* Landw. Jahrb., v. 38, p. 279.

(23) NICHOLS, M. S. 1917 Note on the phenolsulphonic acid method for nitrates in waters containing much magnesium salts. *In* Jour. Indus. and Engin. Chem., v. 9, p. 186–187.

(24) NOYES, H. A. 1919 Accurate estimation of soil nitrates by phenol disulphonic acid method. *In* Jour. Indus. and Engin. Chem., v. 11, p. 213–218.

(25) PERRIER, G., AND FARCY, L. The influence of chlorides on the estimation of nitrates. *In* Bul. Soc. Chim., v. 4, no. 5, p. 178–180; *abs. in* The Analyst, v. 34, p. 174.

(26) POTTER, R. S. AND SNYDER, R. S. 1915 Estimation of nitrates in soil. *In* Jour. Indus. and Engin. Chem., v. 7, p. 863–864.

(27) POUGET, I. 1910 Estimation of nitrites and nitrates by means of phenolsulphonic acid. *In* Bul. Soc. Chim., v. 7, p. 449–452; *abs. in* The Analyst, v. 35, p. 371–372.

(28) PURVIS, J. E., AND COURTAULD, R. M. 1908 The limitations of the copper-zinc couple method in estimating nitrates. *In* Proc. Cambridge Phil. Soc., v. 14, p. 441–446; *abs. in* The Analyst, v. 33, p. 291–292.

(29) RUSSELL, E. J. 1921 Soil conditions and plant growth, 4th ed., p. 348–349. Longmans, Green Co., N. Y.

(30) STEWART, R., AND GREAVES, J. E. 1910 Influence of chlorine upon the determination of nitrates by the phenol disulphonic acid methods. *In* Jour. Amer. Chem. Soc., v. 32, p. 756–757.

(31) STEWART, R., AND GREAVES, J. E. 1912 Production and movement of nitric nitrogen in soils. *In* Centbl. Bakt. (etc), Abt. 2, v. 34, p. 119.

(32) STEWART, R. and PETERSON, W. 1917 Further studies of the nitric nitrogen content of the country rock. Utah Agr. Col. Exp. Sta. Bul. 150.

(33) SYME, W. A. 1909 The colorimetric estimation of nitrates in soil solutions containing organic matter. *In* Jour. Indus. and Engin. Chem., v. 1, p. 188–189.

(34) ULSCH, K. 1890 Eine Methode zur Bestimmung der Salpetersäure durch Reduktion derselben zu Ammoniak. *In* Chem. Centbl., Jahrg. 61, v. 2, p. 926–927.

(35) WAHNSCHAFFE, Felix 1903 Anleitung zur wissenschaftlichen Bodenuntersuchung, 2d ed., p. 105. Paul Parey, Berlin.

(36) WAYNICK, D. D. 1918 Variability in soils and its significance to past and future soil investigations. I. A statistical study of nitrification in soil. Univ. Cal. Pub. Agr. Sci., v. 3, no. 9, p. 243–270.

(37) WHITING, A. L., RICHMOND, T. E., AND SCHOONOVER., W. R. 1920 Determination of nitrates in soil. *In* Jour. Indus. and Engin. Chem., v. 12, p. 982–984; *abs. in* The Analyst, v. 45, p. 460–461.

(38) WHITING, A. L., AND SCHOONOVER, W. R. 1920 Nitrate production in field soils in Illinois. Univ. Ill. Agr. Exp. Sta. Bul. 225, p. 62.

(39) WOLKOFF, M. I. 1916 Studies on soil colloids. I. Flocculation of colloidal solutions. *In* Soil Sci., v. 1, p. 585–601.